The University Tutorial Series.

AN INTRODUCTION TO THE CARBON COMPOUNDS

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The University Tutorial Series.

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AN INTRODUCTION
TO THE
CARBON COMPOUNDS.

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The University Tutorial Series.

AN INTRODUCTION
TO THE
CARBON COMPOUNDS.

INCLUDING THOSE SET IN THE SYLLABUS OF THE INTERMEDIATE
SCIENCE AND PRELIMINARY SCIENTIFIC EXAMINATIONS
OF LONDON UNIVERSITY AS WELL AS THOSE OF
THE FIRST M.B. SYLLABUS OF THE
UNIVERSITY OF CAMBRIDGE.

BY
R. H. ADIE, M.A., B.Sc.,
LECTURER IN CHEMISTRY, ST. JOHN'S COLLEGE, CAMBRIDGE.

Second Impression.

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PREFACE.

A TEACHER of Chemistry sometimes finds it difficult to induce those of his students who are studying the physiology of animal and plant life for Science and Medical degrees to regard organic chemistry with the attention it warrants. The importance to the student of physiology of a subject which helps him to understand the chemical changes brought about by living matter, and the discussions arising therefrom, make it at any rate worth while to try to furnish him with a small work on the elements of the subject treated in as simple a manner as possible; at the same time it is necessary in the case of the science student to impress and emphasize the fact that organic chemistry is just as much a practical experimental subject as inorganic. With this in view, in a book of which the dimensions cannot be considered formidable, an attempt has been made to lead the student to a consideration of the more important groups of carbon compounds by using familiar compounds as far as possible, without laying too great stress on general methods, and it is hoped that he will work through the experiments as he reads the book. Such details are given as will enable him to do this with occasional assistance from a teacher. By this means will be gained a practical familiarity with the chemical relations and properties of the chief classes of compounds which may be studied later from other points of view.

The actual compounds examined and described have been selected to cover the carbon compounds of the Intermediate Science and Preliminary Scientific syllabus of London University as well as those of the First M.B. syllabus of the University of Cambridge.

R. H. Adie.

Cambridge,
February, 1899.

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AN INTRODUCTION TO THE CARBON COMPOUNDS.

CHAPTER I.

INTRODUCTORY.

1. ORGANIC chemistry may be considered as essentially the chemistry of a limited number of elements, viz., those which enter into the composition of all living matter, carbon, oxygen, hydrogen, and nitrogen, but these four by the variety of their compounds, make up for the smallness of their number.

2. Again, in this subject we deal for the most part with molecules, so that we must remind ourselves of a few of the more important points in the Molecular and atomic theory. We have first the two definitions of a molecule: (i) *A molecule is the smallest portion of any substance which is capable of existing in a free state*; (ii) Clerk Maxwell's definition:—*A gaseous molecule is that minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the gas.*

3. This may be followed by the important generalisation of Avogadro, or Avogadro's Law, which is simply stated thus:—*Equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules.* The deduction from this law which connects the molecular weight of a body with its vapour density on the scale in which hydrogen is taken as unity is most important.

Thus, if there be (n) molecules each of a mass (m_1) grammes in unit volume of any gas at 0°C. and 760 mm., then its density (= mass of 1 c.c.) under those conditions equals $n \times m_1 = d_1$. Similarly, for any other gas of density (d_2) there will be (n) molecules each of mass (m_2) grammes in the same volume under the same conditions. Hence, since $d_1 = nm_1$ and $d_2 = nm_2$

$$\frac{d_1}{d_2} = \frac{nm_1}{nm_2} = \frac{m_1}{m_2}.$$

Now, in chemistry we actually use as our unit of mass, the mass of 11,100 cubic centimetres of hydrogen (= 1 gm.), and we also use as our unit of molecular weights the mass of 22,200 c.c. of hydrogen reckoned as 2. By substituting these values for d_2 and m_2, we have

$$\frac{d_1}{1} = \frac{m_1}{2} \text{ or } m_1 = 2d_1.$$

That is the molecular weight of any gas on the scale in which the molecular weight of hydrogen equals 2, is twice the density expressed in the scale in which the mass of 11,100 c.c. of hydrogen equals 1.

4. Hence, in dealing with the chemistry of molecules it becomes of the utmost importance to be able to determine densities of vapours or *vapour densities.*

Now, since $\text{mass} = \text{volume} \times \text{density},$

or $\text{density} = \frac{\text{mass}}{\text{volume}},$

it will be seen that we can either (i) measure out a known volume of a vapour and determine its mass, or (ii) weigh out a known mass and determine the volume it occupies in the state of vapour. The former is the method of Dumas, the latter of Victor Meyer.

Exp. 1.—Dumas' method. Take a bulb or Florence flask with its neck drawn out in the blowpipe flame to a long fine tube, clean it and weigh it ($= w_1$). Read the temperature ($= t°$) and barometric pressure ($= p$ mm.). Warm the bulb and place the open end under a few c.c. of chloroform in a dish. When some of the chloroform has been sucked back into the bulb, warm and repeat the operation until the bulb is about one-tenth full. Hold the bulb under the surface of some boiling water (at 100°) and watch the liquid in the bulb. It boils, drives out the air and gradually distils out of the bulb. As soon as every drop of liquid has gone and the vapour stops rushing out of the tube, seal the end of the tube by a flame, allow the bulb to cool, clean and weigh ($= w_2$). To measure the volume of the bulb, break the end of the tube off under water and allow the bulb to fill with water, weigh again together with piece of glass broken off ($= w_3$).

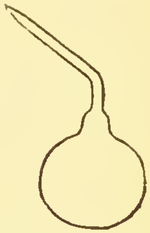


Fig. 1.

Then $w_3 - w_1 =$ weight of water contained in bulb $=$ volume of bulb $= v_1$ c.c.

Calculate the weight of v_1 c.c. of air at $t°$ and p mm. $= w_4$.

Then weight of glass of bulb $= w_1 - w_4 = w$, and the weight of v_1 cc. of chloroform vapour at 100° and p mm. $= w_2 - w$.

Calculate the volume of v_1 c.c. at $t°$ and p mm. $= v_2$, which is the volume occupied by $w_2 - w$ grammes of chloroform vapour at $t°$ and p mm.

Then specific gravity of chloroform vapour (air$=1$)

$$= \frac{w_2 - w}{v_2} \times \frac{v_1}{w_4}$$

and vapour density ($H = 1$)

$$= \frac{(w_2 - w)\, v_1}{v_2 \times w_4} \times 14{\cdot}4.$$

The molecular weight* ($H = 2$) is thus

$$= \frac{(w_2 - w)\, v_1}{v_2 \times w_4} \times 28{\cdot}8.$$

---

* The above steps have been given in preference to a formula as on the whole more practical and requiring less effort of memory.

This method is applicable to solids, liquids and gases, and by appropriate adjustment of the temperature of the bath, to bodies whose vapours decompose at a temperature only a little above their boiling point.

5. **Exp. 2.**—Victor Meyer's method. The apparatus consists of a glass tube *A* about 60 cm. long and 5 mm. bore, one end of which is enlarged into a cylindrical bulb about 15 cm. long and 20 mm. bore. The other end is corked and a delivery tube *BC* is blown into the side of the main tube about 10 cm. from the corked end. The tube is supported vertically with the bulb in a larger tube *D* in which a liquid of higher boiling point than the substance, is boiled. Put some water in the outer tube *D* and boil it. Take a very small bulb, made by drawing out a piece of glass tube very fine, weigh it ($= w_1$) and fill it with ether as in Exp. 1. Weigh it again ($= w_2$). The difference between the weighings is the weight of ether whose volume we are to determine the state of vapour ($= w_2 - w_1$).

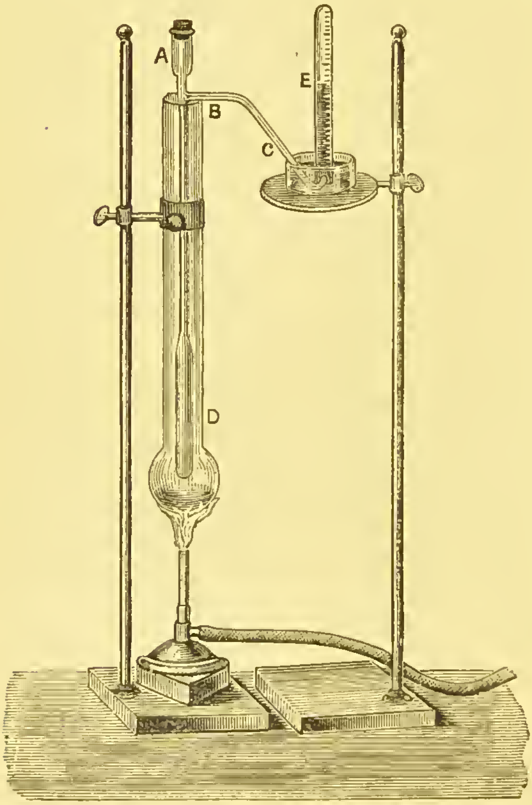


Fig. 2.

When bubbles of air have ceased to rise from the end of the delivery tube which is immersed in water, place a gas measuring-tube, *E*, filled with water over the end. Remove the cork, drop the weighed tube and ether into the bulb, and replace the cork as quickly as possible. In a few moments the ether evaporates and expels air which collects in the gas tube. When the air has been expelled remove the cork, allow the gas tube to cool and read the volume of the gas (v_1) and its temperature ($t°$) and pressure. Correct this volume for temperature, pressure, pressure of water vapour at $t°$, calculate the weight which this corrected volume ($= v_2$) of hydrogen would weigh and divide the weight of ether taken by the weight of the equal volume of hydrogen. Thus

$$\text{vapour density } (\mathrm{H} = 1) = \frac{w_2 - w_1}{v_2} \times 11{,}100.$$

This method is applicable to solids and liquids which are not easily decomposable, and can be used with any gas in the bulb, *e.g.* air, nitrogen, hydrogen, etc. The temperature of the bulb must be some degrees higher than the boiling point of the body whose vapour density is being determined, and water, aniline, oil, sulphur, or fusible alloy are used to heat it.

[Other methods based on the Raoult method are used in the case of bodies which cannot be vaporised without decomposition, but which are soluble. See *Tutorial Chemistry*, Part II., p. 76 *et seq.*]

6. A consideration of the volume changes in the reactions of gases leads to the recognition of the existence of smaller parts within the molecules, viz., the *atoms*, so that molecules are built up of atoms held together by some attractive force which for want of more definite information we call chemical affinity.

Now some molecules only contain two atoms, *e.g.* H_2, Cl_2, HCl, O_2, and in these we can only assume that each atom acts on the other, but in the case of other molecules with three or more atoms, *e.g.* O_3 and H_2O, we have greater possibilities, as each atom may attract both others or one may attract the other two. We get out of this difficulty when we look more closely into molecular compositions and notice that a single hydrogen or chlorine atom is never combined with more than one other atom. We also notice that one oxygen atom generally combines with two other atoms, one nitrogen atom with three or five others, and one carbon atom with four others. We call this property of atoms, their *valency*, and we agree to define it as a number representing the maximum number of atoms which the atom we are considering can hold together to form a molecule. The atoms of chlorine and hydrogen are thus our *standard monovalent atoms.*

The question of valency is of the utmost importance in organic chemistry, as the whole question of the existence of such numbers of carbon compounds is connected with that of valency.

[We also find that there is some difference of opinion as to whether valency should be considered constant or variable. Much has been written on the subject. We shall have to refer to it later.]

CHAPTER II.

ORGANIC COMPOUNDS. PURIFICATION AND ANALYSIS.

7. The number of organic compounds available for investigation is so large that it is difficult to decide at what point to begin. We have plant and animal structures which are obviously mixtures; we have the direct products of living matter both soluble and insoluble in water, *e.g.* starch, sugar, essential and other oils, etc. We have also products of fermentation and putrefaction, *e.g.* spirit, vinegar, &c., but we should perhaps expect that the products obtained from organic compounds by the action of heat, *destructive distillation*, are likely to be simpler in character than those from which they are derived. We meet such products in the cases of coal, oil shale, petroleum, and wood distillation.

8. These natural organic compounds are generally impure and it becomes necessary to purify the bodies before attempting to identify them. The operations are on the whole as general as the methods available in inorganic chemistry. Thus we employ *distillation*.

Exp. 3.—Place a mixture of methylated spirit and water (half and half), in a distilling flask connected with a condenser, and provided with a cork through which a thermometer is fixed, at such a distance that its bulb is just below the side exit tube. Support the apparatus by a retort stand, place a burner under the flask and a receiver under the end of the condenser tube, and note the rise of the thermometer. When the liquid boils it rises at once to about 79·5° and remains at that point for a short time, it then gradually rises until it reaches nearly 100°. Change the receiver when the temperature begins to rise above about 85°, and again at about 99°. In this way the mixture is separated into three parts or fractions which boil at different temperatures. Try to light some of the original and the fractions. The first fraction only burns and contains the greater part of the spirit.

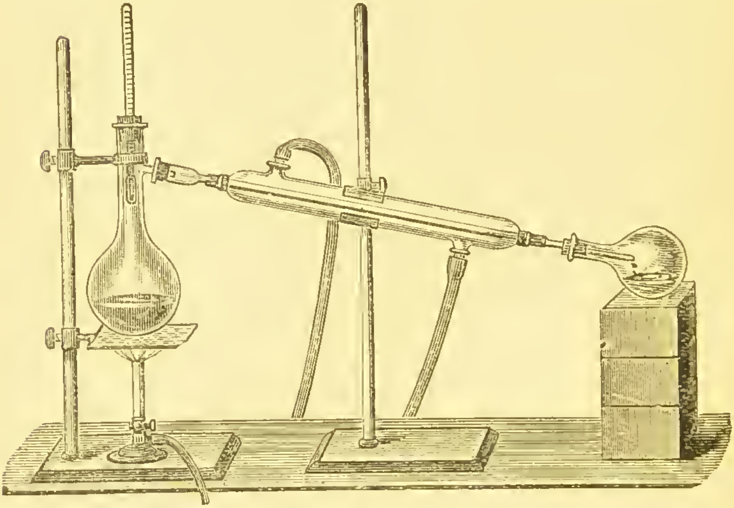


Fig. 3.

The process just described is called *fractional* distillation, and is largely used in separating mixtures of liquids.

9. The method of purification by solution and filtration or crystallisation, is similar to that in use in inorganic work, except that the number of solvents available is much greater in organic work. In addition to water, alcohol, ether, chloroform, acetic acid, benzene, petroleum and sometimes glycerin, are used. Since these bodies are not equally soluble in each other, separation is sometimes effected by taking a substance which is dissolved or disseminated in one liquid out of that liquid by means of another liquid, *i.e.* the method of *extraction* by shaking with ether or chloroform.

Exp. 4.—Place some milk in a cylinder and add to it some caustic soda solution and some ether, and shake well up. Allow it to stand; in a short time the ether will rise to the surface with the dissolved fat. Pipette off a few drops and put on blotting paper. The drops evaporate, leaving a grease spot behind.

10. The tests which are available for the bodies separated by any method are quite general, and consist in the first place of the characteristic reactions of the chief elements.

Exp. 5.—Take some powdered pure copper oxide, heat it to redness in a crucible, and allow it to cool in a dessicator. Mix with it a little sugar and heat the mixture in a hard glass tube. Note that water (tested by anhydrous copper sulphate which it turns blue) is formed from sugar and the dry oxide, a proof of the presence of *hydrogen.* Lower a drop of lime water into the tube on a glass rod; it is turned milky, hence carbon dioxide is present, which must have come from *carbon* in the sugar.

Exp. 6.—Take a small piece of gelatine, put it in a test-tube, add a small piece of sodium about the size of a pea and heat. When the action stops put the tube into a larger tube or beaker and add water, ferrous sulphate, ferric chloride, and hydrochloric acid. The formation of a blue colour, *Prussian blue*, shews that nitrogen has been contained in the gelatine. (See p. 77).

Sulphur, phosphorus and the halogens may be identified by fusing some of the substance with potassium nitrate and then testing for a sulphate, phosphate or haloid salt, respectively.

Exp. 7.—Take a little white of egg, mix it with potassium carbonate, and heat. When the reaction is over place the residue on a silver coin and moisten with dilute hydrochloric acid, a black stain of silver sulphide shews the presence of sulphur.

11. Modifications of the above methods of testing for the elements are used to determine the quantitative composition of organic bodies. To determine the percentage of carbon and hydrogen, a weighed quantity of the body is mixed with excess of copper oxide and heated in a long glass tube, or it is heated in a stream of oxygen which is then passed over red hot copper oxide. The water and the carbon dioxide formed are collected in a calcium chloride tube and a solution of caustic potash respectively and weighed. Then since 44 grammes of carbon dioxide contain 12 grammes of carbon, and 18 grammes of water contain 2 grammes of hydrogen, the carbon in the weighed substance $= \frac{12}{44} = \frac{3}{11}$ weight of carbon dioxide, and the hydrogen in the weighed substance $= \frac{2}{18} = \frac{1}{9}$ weight of water. In this reaction any nitrogen present is evolved in a free state and may be collected and measured after passing through caustic potash solution to absorb carbon dioxide. The details of organic analysis, *i.e.* the *carbon and hydrogen* and the *nitrogen combustion* are beyond the scope of this work, as are also numerous methods of determining nitrogen, sulphur, phosphorus, the halogens, etc.

12. Having obtained the percentage composition of any body it becomes possible to convert it at once into a molecular composition by the usual steps.

(1) Calculate the composition of an amount of the body which contains one part by weight of hydrogen, or sixteen of oxygen, or twelve of carbon.

(2) Divide the molecular weight by the sum of the components expressed as above, and find the nearest whole number to the quotient.

(3) Multiply the composition (1) by this whole number throughout, and it becomes the molecular composition. [Special cases will be found in § 14 and 21.]

CHAPTER III.

HYDROCARBONS. PARAFFIN SERIES.

13. In starting with a gas prepared by the decomposition of organic matter, *e.g.* coal gas, we test first of all by burning.

> **Exp.** 8.—Collect a cylinder of coal gas (which has been passed over caustic potash to remove carbon dioxide and through sulphuric acid to remove water) by upward displacement and apply a light to it. The gas burns and the product left in the cylinder turns limewater milky. Notice that water is formed as well.

Coal gas then, contains combined carbon, and hydrogen combined or free, perhaps both. If the gas is passed through a long porous tube or over spongy platinum—or better, palladium—about forty per cent. is found to be hydrogen. The residue still forms carbon dioxide and water on burning. If the residual or original gas is allowed to stand over strong sulphuric acid about eight per cent. disappears, but the residual fifty per cent. of the original gas still contains carbon and hydrogen. The properties of this gas are similar to those of a gas prepared from vinegar by heating it with excess of soda lime, or better from sodium acetate by heating it with soda lime.

14. The analysis of this gas, obtained by burning it with red hot copper oxide, gives the following percentage:

$$\begin{array}{lr} \text{Carbon} & = 75{\cdot}00 \\ \text{Hydrogen} & = 25{\cdot}00 \\ \hline & 100{\cdot}00 \end{array}$$

which, when arranged in terms of one part by weight of hydrogen is

$$\begin{array}{lr} \text{Carbon} & = 3 \\ \text{Hydrogen} & = 1 \\ \hline & 4 \end{array}$$

Now the vapour density (hydrogen = 1) of this gas is 8, so that the molecular weight of the gas (hydrogen = 2) is 16, and we must multiply each of the above figures by four to produce a molecular composition, thus

$$\begin{array}{lcl} \text{Carbon} & = 3 \times 4 = 12 & = \mathrm{C} \\ \text{Hydrogen} & = 1 \times 4 = 4 & = \mathrm{H_4} \\ & \overline{4 \times 4} \quad \overline{16} & \end{array}$$

The molecular formula of the gas is thus CH_4, and it is called *marsh gas* or *methane.* As it contains the least possible amount of carbon per molecule, *i.e.* one atom, it is looked upon as the simplest and most fundamental compound of carbon and hydrogen.

Methane or marsh gas is found in nature among the products of fermentation and decay in a limited supply of air, *e.g.* in the decay of vegetable matter under water in stagnant pools, marshes, and bogs. It is also found in coal mines as the explosive fire-damp, and in the natural gas of the oil districts.

Methane is prepared in various ways :—

(1) By the action of soda lime on sodium acetate.

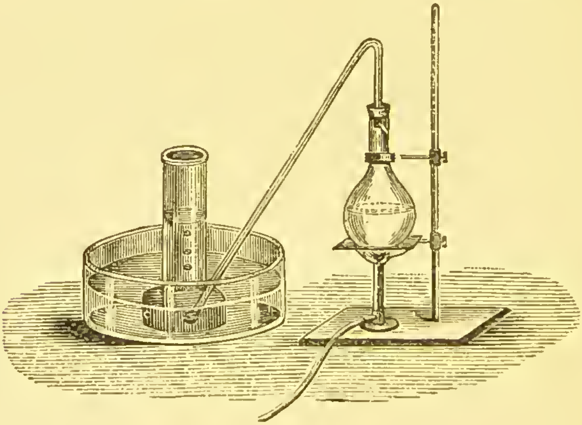


Fig. 4.

Exp. 9.—Put some fused sodium acetate in a hard glass flask with excess of soda lime. Fit with delivery tube and arrange to collect over water (Fig. 4). Heat the flask and collect the gas, after driving out the air. Care must be taken not to fuse the flask locally or to allow condensed water to run back on the hot parts. Notice the colour, taste, and smell of the gas. Prove that it is lighter than air, and that it explodes when mixed with ten times its volume of air in a soda-water bottle. Prepare an extra cylinder for Exp. 10.

(2) By acting on a compound, zinc methyl or sodium methyl by water. This method is available for getting the gas pure.

(3) By the action of a zinc-copper couple on methyl iodide in acidified alcoholic solution.

16. It will be seen that no equations have been given, and it will be well to consider the subject of equations very briefly.

An equation should tell us as far as possible (i) the elements taking part in a reaction, their arrangement before and after, and the weights of the initial and final products; (ii) the volume of any gaseous constituents; and (iii) something (generally not much) about the conditions of the reaction. In inorganic chemistry these requirements are generally fairly fulfilled, but in organic chemistry they are not, because as a rule the product desired is only one of several, and may only represent a very small part of the total products. Any use of equations must hence be subject to this grave defect.

The equations generally given for the above reactions are

$$(1)\quad \underset{\text{Sodium acetate}}{NaC_2H_3O_2} + NaOH = Na_2CO_3 + CH_4$$

Even at this stage this equation suggests that the two carbon atoms in sodium acetate must have different properties.

$$(2)\quad \underset{\text{zinc methyl}}{Zn(CH_3)_2} + 2\,H_2O = Zn(OH)_2 + 2\,CH_4$$

$$(3)\quad CH_3I + H_2 = CH_4 + HI.$$

17. Methane is a colourless tasteless gas with a slight smell of coal gas; it can be liquefied by pressure and low temperature, and boils at −164°. It is about half as heavy as air, its vapour density [hydrogen = 1] being only 8 compared with that of air = 14·4. When mixed with excess of oxygen and exploded, a contraction is observed equal to twice the volume of the gas taken, and caustic potash absorbs from the residue a volume of carbon dioxide equal to the volume of the original gas. An examination of the products of explosion at 100° shows that a volume of steam is formed equal to twice the volume of the original gas, so that 1 c.c. of methane gives rise to 1 c.c. of carbon dioxide and 2 c.c. of steam. Applying Avogadro's Law,

1 molecule of methane gives rise to 1 molecule of carbon dioxide
+ 2 molecules of steam.

Now each molecule of carbon dioxide contains one atom of carbon, and each molecule of steam contains two atoms of hydrogen, and there is no oxygen in marsh gas,

∴ 1 molecule of methane contains 1 atom of carbon
+ 4 atoms of hydrogen,

and is represented by the formula CH_4. This gives another and independent proof of the composition of methane.

18. In addition to oxygen other reagents are used:—

(*a*) Chlorine:—

Exp. 10.—Mix a cylinder of methane with an equal volume of chlorine. White fumes are seen in daylight and the mixture explodes. The mixture also explodes under the influence of daylight or burning magnesium wire. The chlorine disappears and fumes of hydrochloric acid are seen. The products are hydrochloric acid gas, which is readily absorbed by water, and another colourless gas, which is only slightly soluble in water. The gas burns to a mixture of carbon dioxide, steam and hydrochloric acid, and the percentage composition and molecular weight are represented by the formula CH_3Cl, it is called *monochlormethane* or *methyl chloride*.

Bromine and iodine have little or no action on this gas.

(*b*) Hydrochloric acid has no action.

(*c*) Sulphuric and nitric acids have no action unless above 150° and then the action is only slow.

(*d*) Caustic potash has no action.

(*e*) Oxidising and reducing agents do not affect the gas.

Since the molecule of the gas contains four hydrogen atoms combined with one carbon atom, the carbon atom is tetravalent, and it is only possible to obtain derivatives from it by replacing or *substituting* one or more of the hydrogen atoms by other monovalent atoms or groups as in the above case of chlorine. In fact, the repeated action of chlorine yields the bodies CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4 which must be studied later together with the iodine substitution derivatives prepared by other methods.

19. *Syntheses* of methane which connect organic compounds with inorganic may be given here.

(*a*) Hydrogen unites directly with carbon at 1200° to form methane.

(*b*) An electric spark passing between carbon poles in an atmosphere of hydrogen causes the formation of methane to the extent of 2½ to 3 per cent. of the volume of the hydrogen.

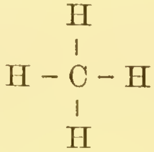
(*c*) A mixture of carbon bisulphide vapour and sulphuretted hydrogen (made by passing sulphuretted hydrogen through carbon bisulphide), when passed over red hot copper loses sulphur, while the carbon and hydrogen combine to form methane. An equation can be written

$$8\,Cu + 2\,H_2S + CS_2 = 4\,Cu_2S + CH_4.$$

20. When the substitution derivatives of methane are carefully examined it is found that only one mono-substitution derivative, *i.e.* a compound formed by substituting one hydrogen atom by one monovalent atom or group, can be prepared. Thus it is possible to replace each of the

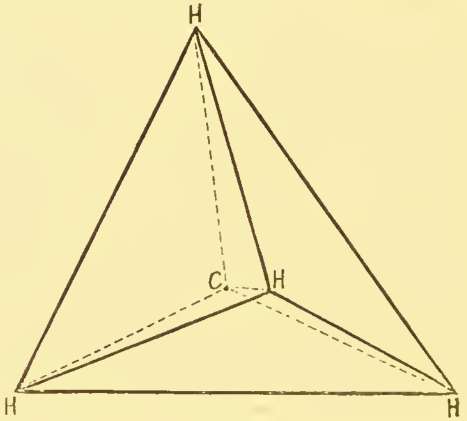
hydrogen atoms in turn by chlorine, and the resulting monochlormethanes are identical.

Hence we assume that all the hydrogen atoms are symmetrically attracted by the carbon atom, and we draw a formula to represent this in one plane, thus



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

or in space by representing the carbon atom as the centre of a tetrahedron formed by the four hydrogen atoms, thus



These are *constitutional* formulae, and are of the greatest use. We must return to them later.

21. Starting with methyl chloride, CH_3Cl, it is possible to prepare an unlimited number of bodies. It is possible to remove the chlorine from the molecule by means of sodium. The methyl chloride is dissolved in ether and sodium is placed in the solution. A gas is given off which resembles methane in its reactions and is called *ethane*. By combustion its percentage composition and the amount required to contain one part by weight of hydrogen are found to be

$$\begin{array}{lrr} \text{Carbon} & = 80{\cdot}00 & = 4 \\ \text{Hydrogen} & = 20{\cdot}00 & = 1 \\ \hline & 100{\cdot}00 & = 5 \end{array}$$

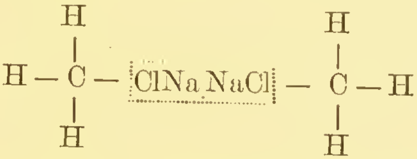
The vapour density $[H = 1]$ is 15, and its molecular weight $[H = 2]$ is 30. Hence its molecular composition is

$$\begin{array}{lcl} \text{Carbon} & = 4 \times 6 = 24 = & C_2 \\ \text{Hydrogen} & = 1 \times 6 = 6 = & H_6 \\ \hline & 5 \times 6 = 30 & \end{array}$$

The formula C_2H_6 may be considered to be derived from CH_4 by (i) the substitution of a group of atoms CH_3 for one hydrogen atom, or (ii) the addition of a group CH_2. The former hypothesis is the only one which is consistent with the tetravalency of the carbon atom, so we must adopt it. Thus

$$CH_3Cl + CH_3Cl + 2\,Na = CH_3 - CH_3 + 2\,NaCl$$

It may also be expressed structurally like this



$$\begin{array}{ccccccc} & H & & & & H & \\ & | & & & & | & \\ H - & C & - & \boxed{ClNa\ NaCl} & - & C & - H \\ & | & & & & | & \\ & H & & & & H & \end{array}$$

22. Ethane is a colourless, tasteless gas with a slight smell. It burns in air and explodes when mixed with air or oxygen. Chlorine acts upon it in sunlight substituting one or more atoms of chlorine for hydrogen atoms as in the case of methane. The most interesting of these derivatives are *ethyl chloride* or monochlorethane C_2H_5Cl and the disubstituted compounds represented by the formula $C_2H_4Cl_2$, see § 43. The other reagents mentioned in § 18 do not attack ethane. Ethane resembles methane still further, the methods of preparing methane being also generally applicable to ethane. These are

i. By distilling sodium propionate a salt which contains three carbon atoms with excess of soda lime

$$NaC_3H_5O_2 + NaOH = Na_2CO_3 + C_2H_6$$

ii. By the action of water on sodium ethyl or zinc ethyl

$$\underset{\text{Zinc ethyl}}{Zn(C_2H_5)_2} + 2\,H_2O = Zn(OH)_2 + 2\,C_2H_6$$

iii. By the action of the zinc copper couple on ethyl iodide in alcoholic solution.

Perhaps the most important of the methods available is that by which we arrived at ethane, viz. the action of sodium on methyl chloride, since that method has enabled us to add a carbon atom to a molecule of a carbon compound.

23. Can we in any way explain the similarity of properties of methane and ethane? Can we connect it with the presence in both their molecules of carbon atoms which are tetravalent, and of tetravalent carbon atoms alone? We shall find as we proceed that there is some such intimate connexion. When the natural oil gas and the natural petroleum oils are distilled they may be separated into a large number of different fractions with approximately constant boiling points. Thus we can isolate bodies having the formulae C_3H_8 *propane*, C_4H_{10} *butane*, C_5H_{12} *pentane*, etc., up to bodies with fourteen or more carbon atoms in the molecule.

The properties of all of these bodies are similar to those of methane and ethane, and they differ in composition by regular amounts of one carbon atom and two hydrogen atoms. The earlier members up to pentane C_5H_{12} are gases at ordinary temperatures, from pentane to decane are liquids and with a higher carbon content they become waxy solids. Such a series of bodies is called a *homologous series*, and this series is called the *paraffin series* since the members are so difficult to attack by reagents.

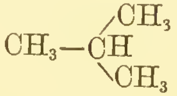
It will be noticed that the series is built up of carbon and hydrogen atoms, of which the hydrogen atoms are monovalent, so that they are held together by the attraction of each carbon atom for other carbon atoms. It is this extraordinary peculiarity of the carbon atom of combining with itself and forming new compounds, generally called *atom linking*, which makes the subject of carbon chemistry at the outset contrast so strongly with inorganic chemistry.

24. Having once gained the idea that molecules can be built up by the linking of carbon atoms we are able to explain a further peculiarity noticed in the compounds of the paraffin series. When the hydrocarbons containing

four or more carbon atoms are examined carefully, it is noticed that they have not always the same properties even with the same percentage composition and molecular weight. Thus in the case of *butane* C_4H_{10} we find two bodies with different boiling points, $-17°$ and $+1°$ and forming different series of substitution derivatives. Can we explain this in any way?

An examination of the formula C_4H_{10} shows that it can be arranged in two ways and in two ways only, so as to keep the carbon atoms tetravalent and the hydrogen atoms monovalent: the two formulae are

$CH_3—CH_2—CH_2—CH_3$ and



$$CH_3—CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix}$$

The former would be called *normal butane*, the latter *isobutane*. The existence of the two hydrocarbons and the two series of compounds is certainly explained by the hypothesis of valency and the existence of the two formulae deduced on that hypothesis. The two butanes are said to be *isomers*, and we define this phenomenon of *isomerism* thus:—When two compounds have the same percentage composition and molecular weight, *i.e.* the same molecular formula, but different properties, they are said to be *isomeric* with each other.

25. It should be noted that the natural oils and oil gas yield a large number of paraffins in their different fractions, thus the oil gas contains methane to butane and pentane; gasoline and benzoline contain pentane to heptane; paraffin oil contains heptane to decane and paraffin wax contains tetradecane and upwards. All these hydrocarbons and their isomers can be prepared by methods which are applicable to all. Thus we can (i) add one or more carbon atoms to any hydrocarbon by acting on a mixture of its monochlor derivative and methyl chloride (or iodide) by sodium, or (ii) take away one carbon atom by distilling a salt of the acid formed from the hydrocarbon with soda lime.

CHAPTER IV.

HYDROCARBONS (CONTINUED):—ETHYLENE, ACETYLENE, BENZENE.

26. In the last chapter we removed chlorine from methyl chloride CH_3Cl by the action of sodium. We shall now try to remove it by the action of the hydroxide of sodium caustic soda.

Exp. 11.—Take a small flask fitted with thistle funnel, cork and delivery tube for collection over water. Place in the flask some alcohol and caustic soda or potash and warm it. Pour in a few drops of methyl or ethyl iodide by means of the funnel and collect two cylinders of the gas which comes off. Apply a light, the gas burns. Place one of the cylinders containing the gas over a cylinder of chlorine. The two gases combino and form oily drops.

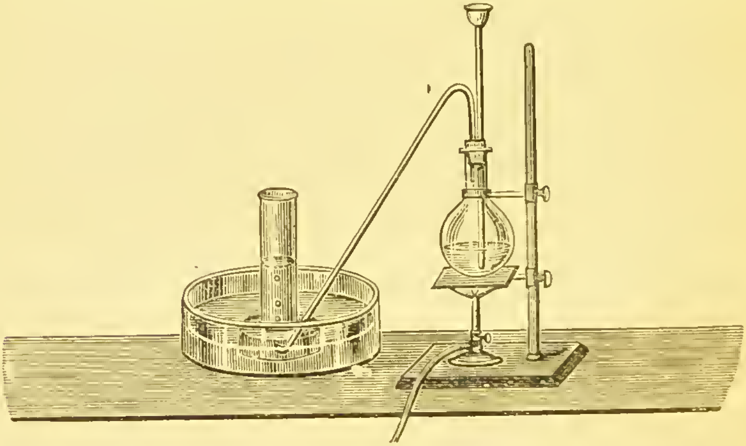


Fig. 5.

By the action then, of caustic alkali on methyl or ethyl iodide we form a gas which is unlike ethane since it reacts directly with chlorine to form an oily compound. The percentage composition and molecular weight are found to indicate the formula C_2H_4, and the gas is called *ethylene*

27. Ethylene is generally prepared from alcohol by the action of sulphuric acid. The reaction is most important and will be discussed later, but briefly, the formation of ethylene is due to the decomposition of a salt, ethyl hydrogen sulphate, which is formed by the reaction between the sulphuric acid and alcohol. The reaction may be represented by the equations

$$\left\{\begin{array}{l} C_2H_6O + H_2SO_4 = \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5 \, . \, HSO_4} + H_2O \\ C_2H_5 \, . \, HSO_4 = C_2H_4 + H_2SO_4 \end{array}\right.$$

Exp. 12.—Make a mixture of 10 c.c. of alcohol [methylated spirit], 10 c.c. of water, and 30 c.c. of strong sulphuric acid, and place it in a glass flask fitted with a thistle funnel and a delivery tube for collecting over water. (Fig. 5.) Heat the mixture to about 165°. It froths and gives off ethylene gas. Collect four or five cylinders of the gas.

(*a*) Turn one cylinder up and remove the cover. In a few seconds apply a light to it. The gas burns, it is not light enough to rise very quickly in air.

(*b*) Place one cylinder over a cylinder of equal size filled with chlorine. The gases disappear without forming hydrochloric acid and appear as oily drops (Dutch liquid).

(*c*) Drop a drop of bromine into another cylinder. The red colour disappears and oily drops are again formed.

(*d*) Stand another cylinder over strong sulphuric acid. The gas is slowly absorbed by the acid.

Ethylene is a colourless gas with a slightly sweet spirituous taste and smell. It boils at − 103°. It burns in air with a more luminous flame than methane, and explodes when mixed with three times its volume of oxygen. It combines directly with its own volume of chlorine or bromine vapour to form $C_2H_4Cl_2$ and $C_2H_4Br_2$ dichlor- and dibrom-ethane or *ethylene dichloride* and *dibromide* respectively. Ethylene combines slowly with hydrochloric acid and rapidly with hydriodic acid to form ethyl chloride and iodide, respectively; it combines with sulphuric acid forming ethyl hydrogen sulphate. Oxidising agents oxidise it and reducing agents reduce it to ethane.

28. The characteristic differences between the properties of ethylene and ethane are accompanied by a difference in composition. Ethylene contains two atoms of hydrogen per molecule less than ethane, and its molecule is able to take up two other monovalent atoms or groups but no more, in the place of the missing hydrogen atoms. The difference is best summarised by considering that the two carbon atoms of the ethylene molecule are trivalent, so that they can take up two other monovalent atoms or groups and thus become tetravalent. On this account ethylene is called an *unsaturated* hydrocarbon.

A convention has been almost universally adopted to express the existence of a pair of trivalent carbon atoms, viz.: a double bond, so that ethylene may be given the two formulae

$$\underset{\text{Trivalent carbon atoms}}{H_2C''' - C'''H_2} \quad \text{and} \quad \underset{\text{Double bond}}{H_2C = CH_2}$$

[The practical conveniences of using the double bond symbol may outweigh the objection to a name which suggests that the mode of attraction symbolised by a double bond should be stronger than that indicated by a single bond, whereas the opposite is the case.]

The fact that unsaturated carbon atoms can only exist in pairs explains why no compound CH_2 can be prepared from methyl chloride, since the unsaturated carbon atoms immediately pair off and form ethylene, $CH_2 - CH_2$.

Just as in the case of methane and ethane, a whole series of homologues of ethylene exists, forming the *olefine series.* The characteristic property of this series is the formation of addition compounds by union with two monovalent atoms or groups.

29. To proceed with our investigations, when we try the effect of removing chlorine or bromine from the molecules of ethylene dichloride or dibromide by the action of a caustic alkali in alcoholic solution, we find that a new gas is produced with a characteristic smell [that of a Bunsen burner burning back]. It is found to be represented by the molecular formula C_2H_2 and is called *acetylene.*

The same gas is formed, mixed with marsh gas, when electric sparks are passed between carbon poles in an atmosphere of hydrogen or of marsh gas, and the product contains 10 per cent. of acetylene and 2·5 to 3 per cent. of marsh gas in excess of hydrogen. A more convenient method of preparing the gas is by the action of water on calcium carbide CaC_2, a product of heating quicklime with carbon in the electric furnace.

Exp. 13.—Take a pneumatic trough of water and drop in a lump of calcium carbide. Cover the lump with an inverted cylinder of water and collect the gas. Notice the colour, taste, and smell of the gas. Test it with a light, it burns with a bright smoky flame.

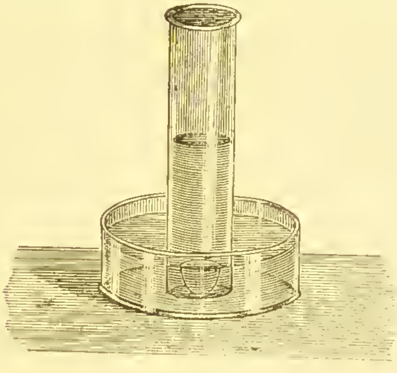


Fig. 6.

Pour into one cylinder some cuprous ammonium chloride solution (Made by boiling copper oxide with hydrochloric acid and copper filings. Pour the product into water, allow the white precipitate to settle, pour off most of the liquid and add ammonium chloride until the precipitate dissolves), and add a few drops of liquor ammonia; a bright red precipitate is immediately formed.

30. Acetylene is a colourless gas with characteristic taste and smell. It boils at 0^0 under a pressure of 21·5 atmospheres. It dissolves in its own volume of water. It unites directly with chlorine, bromine, hydrochloric acid, hydrobromic acid, and sulphuric acid to form addition products by combining with two or four monovalent atoms or groups; of these products $C_2H_2Br_4$, acetylene tetrabromide is the most often used. Acetylene burns in air and explodes when mixed with air or oxygen, and occasionally it detonates violently. (Hence it is dangerous to attempt to explode the mixture.) When delivered from a small orifice, *e.g.* a gas burner, it forms a very luminous flame and so it is used to enrich coal gas. It forms a red compound with cuprous chloride, *cuprous acetilide*, Cu_2C_2 which is decomposed by the action of acids, acetylene being again set free. Acetylene is formed when hydrocarbons burn in an insufficient supply of air or oxygen.

Exp. 14.—Take a dry cylinder, invert it over a Bunsen burner burning at the bottom. In a few seconds nearly close the cylinder with a glass plate and pour in a small quantity of cuprous ammonium chloride solution. Shake up well and then pour one or two drops of ammonia solution down one side of the cylinder; a red precipitate is formed showing the presence of acetylene in the products of combustion.

Acetylene is a poisonous gas combining like carbon mon oxide and nitric oxide with the haemoglobin of the blood.

31. The properties and composition of this gas are best summarised in the symmetrical structural formulae

$$HC'' - C''H \quad \text{and} \quad HC \equiv CH$$

which contain a pair of divalent carbon atoms and a pair of carbon atoms united by a triple bond, respectively. As in the case of ethylene the latter symbol is more generally used though the objection to its use is similar in both cases. When bromine combines directly with acetylene, forming acetylene tetrabromide, the carbon atoms again become tetravalent, or the triple bond is broken. Acetylene like ethylene is the first member of a series of unsaturated homologues, the *acetylene* or ethine *series.*

32. Since the carbon atom is only tetravalent it is useless to proceed at present in the direction of removing more hydrogen atoms from its simpler compounds, so we return now to the liquid product of the distillation of coal, the *coal tar.*

In the fractional distillation of coal tar a rough separation of the distillate is made by collecting it in water. Part floats, the light coal tar naphtha, and when this is redistilled a considerable fraction is collected in the form of a liquid, boiling between 80° and 82°. When lit it burns, forming carbon dioxide and water and nothing else (except carbon in the form of soot). Its percentage composition and molecular weight are represented by the formula C_6H_6 and it is called *benzene* or *benzol.*

33. Chlorine acts fairly readily on benzene in the cold, or more readily in presence of iodine. Fumes of hydrochloric acid are given off, and the product obtained contains chlorine atoms substituted for hydrogen atoms. Now the formula suggests that the carbon atoms cannot all be tetravalent, or that some of them must be connected by double bonds, *i.e.* that the carbon atoms are unsaturated, and it is hardly to be expected that an unsaturated body of the character of ethylene or acetylene would form substitution instead of addition products. In sunlight, however, addition of chlorine does take place, and the addition is limited to six atoms forming $C_6H_6Cl_6$, benzene hexachloride. This body easily splits off hydrochloric acid on heating, forming $C_6H_3Cl_3$, trichlor-benzene.

Hydrochloric acid has no action on benzene, presenting another contrast with ethylene.

Hydriodic acid has no action on benzene unless heated with it in a sealed tube, when two, four, or six hydrogen atoms may be added, forming bodies of the formulae C_6H_8, C_6H_{10}, and C_6H_{12}. The strongest hydriodic acid under the same circumstances can even add eight hydrogen atoms, but the product is now identical with a hexane, C_6H_{14}, a characteristic paraffin, and it has lost its characteristic benzene properties.

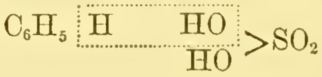
34. Nitric acid has a remarkable and characteristic action.

Exp. 15.—Take a small flask and put into it a mixture of 35 c.c. strong nitric acid with 40 c.c. concentrated sulphuric acid. Drop into the mixture a few c.c. (not more than 20 c.c.) of benzene, taking great care to add it gradually, to keep it well shaken up, and to keep the flask cool; when all the benzene has been added warm to about 60°. The benzene becomes yellow and acquires a smell of bitter almonds. Pour the mixture into water, separate the yellow oil, dry it by calcium chloride and distil it (Fig. 3). Any unchanged benzene distils over first, but the boiling point of the mixture rises and a fraction is collected, boiling at about 210°.

The product is a yellow liquid with a characteristic smell of almonds, and boiling at 210°. Its analysis suggests the formula $C_6H_5NO_2$, and its molecular weight agrees with this formula. It is called *nitro-benzene*, the group $—NO_2$ which replaces one atom of hydrogen in the benzene being called the *nitro group*. In this case it appears that the substitution of a nitro group in benzene is attended by a reduction of the nitric acid to the nitrous state, the hydrogen of the benzene combining with the hydroxyl of the acid to form water. Thus the greater part of the reaction may be represented by the equation

$$C_6H_6 + NO_2OH = C_6H_5NO_2 + H_2O$$

Sulphuric acid has a similar reaction when heated with benzene for some time. A body of the formula $C_6H_5 . SO_3H$ *benzene sulphonic acid* or *sulphobenzene* is formed, which contains one atom of hydrogen replaceable by the metal of a base. It is an acid formed by reducing sulphuric acid by the hydrogen of benzene, water being formed as well, thus



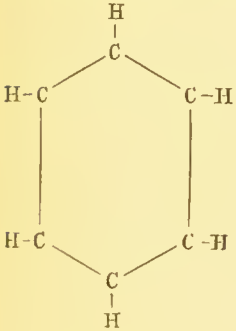
$$\begin{array}{l} C_6H_5\,\boxed{H \qquad HO} \\ \qquad\qquad\quad HO \end{array}\!\!> SO_2$$

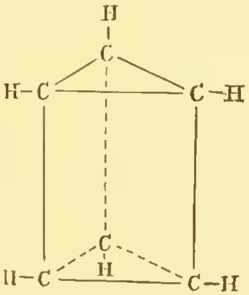
or expressed in the form of an equation

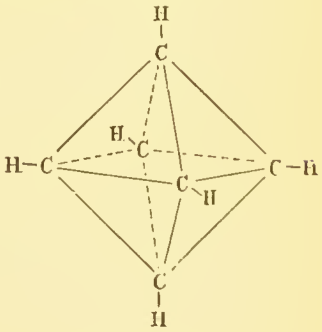
$$C_6H_6 + SO_2(OH)_2 = C_6H_5 . SO_3H + H_2O$$

Weak solutions of alkalies and acids have no action on benzene, nor have metals in the cold. Oxidising agents form bodies with two or more hydrogen atoms replaced by oxygen.

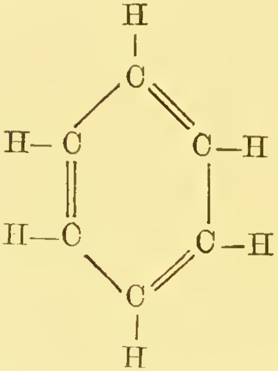
35. In the case of benzene then, we have to explain these facts, (i) from its formula we should expect it only to form addition compounds, yet it forms substitution compounds in the cases of chlorine, nitric acid, and sulphuric acid. (ii) From its formula we should expect to be able to add eight hydrogen atoms or chlorine atoms in order to make all the carbon atoms tetravalent, yet we find it is difficult to add more than six such atoms and with the final addition of the last two we get an abrupt change of properties to those of a paraffin. (iii) The six carbon atoms always keep together as long as the properties are characteristic of benzene. (iv) The six hydrogen atoms seem to be symmetrically situated in the molecule, since we can prepare six monochlor benzenes in which each hydrogen atom is sustituted in turn and they are all identically the same. The most probable induction from these facts is that the carbon atoms are symmetrically connected. Three formulae have been drawn among others which fufil these conditions, viz. (*a*) a ring or hexagon, suggested by Kekulé, (*b*) a prism, suggested by Ladenburg, and (*c*) an octahedron, suggested by Thomsen. Thus







Of these formulae the first (*a*) is the one which best fulfils the conditions, though it represents a plane instead of a space relation of the atoms. It may also be arranged to indicate that the carbon atoms are all trivalent or are connected alternately by double bonds, thus:—



It shows that hydrogen atoms can be added in pairs of two, four, or six, making pairs of carbon atoms directly attracted by each other in the ring tetravalent, or severing a double bond, and it shows that the addition of eight monovalent atoms can only take place by splitting the ring, which allows two extreme atoms to be added at the expense of the loss of the ring structure.

It would be well to remind ourselves that a *structural formula* is principally a convenient shorthand for embodying facts and reactions, and may not represent any known arrangement of the atoms within the molecule.

Hydrocarbons, which we assume to be built up on the plan of benzene with a closed chain of carbon atoms, are said to have a *cyclo structure,* in distinction to those which have an *open chain structure.*

36. Two other methods of preparing benzene should be mentioned.

Exp. 16.—Take a few grammes of sodium benzoate and heat it in a test-tube with excess of sodalime. (Fig. 7.) Drops of a liquid are formed, which have the properties of benzene.

The reaction between a benzoate and an alkali may be expressed by means of an equation which represents part of the reaction, and indicates the similarity between this method of preparation and that of preparing the paraffins.

$$\underset{\text{Sodium benzoate}}{C_7H_5O_2Na} + NaOH = Na_2CO_3 + C_6H_6$$

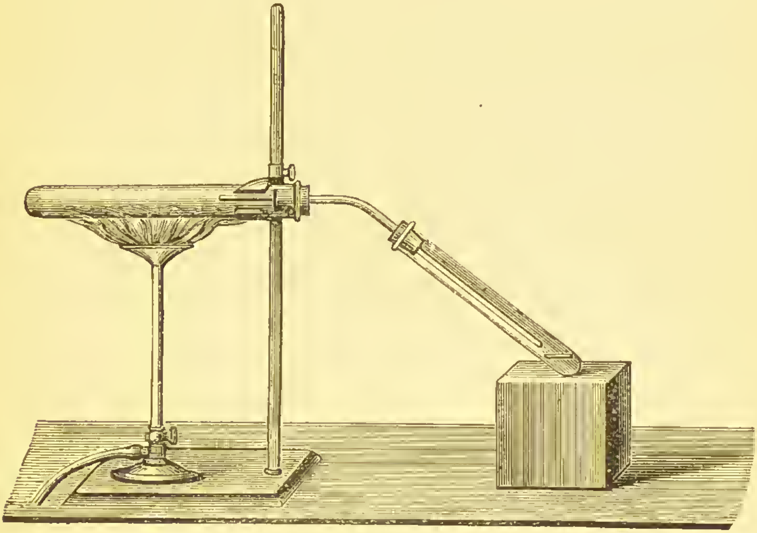


Fig. 7.

The second method is to pass acetylene through a red hot tube. The molecules of acetylene join together and form bodies of the formulae C_4H_4, C_6H_6 and C_8H_8.

The C_6H_6 is benzene, and it will be noticed that its percentage composition is the same as that of acetylene though its molecular weight is three times as great. Now, when we have two bodies with the same percentage composition, but different molecular weights, the body with tho higher molecular weight is said to be a *polymer* of the other. Sometimes the polymer has properties which are similar to those of the original, but sometimes, as in this case, the properties are very different. The phenomenon is termed *polymerism.*

37. Just as we can substitute hydrogen atoms in open chain hydrocarbons by hydrocarbon groups, so we can do

the same in the case of benzene. The resulting bodies combine the properties of both nucleus and substituted groups.

The first of these derivatives of benzene formed by replacing one hydrogen atom by a methyl group is also found in coal tar, and is called *toluene*, $C_6H_5CH_3$. It is obtained from the fraction boiling between 110° and 112°, and has a boiling point of 110°.

CHAPTER V.

HALOID DERIVATIVES. CHLOROFORM.

38. Several of the haloid derivatives of methane are both interesting and important. As we have seen already, the action of chlorine on marsh gas forms in succession

Monochlormethane or methyl chloride.	CH_3Cl.
Dichlormethane or methylene dichloride.	CH_2Cl_2.
Trichlormethane or chloroform.	$CHCl_3$.
Tetrachlormethane or carbon tetrachloride.	CCl_4.

Methyl chloride, CH_3Cl is more readily prepared by heating wood spirit, methyl alcohol, with concentrated hydrochloric acid under pressure, a reaction which may be represented by the equation

$$CH_4O + HCl = CH_3Cl + H_2O$$

It is a gas liquefiable by pressure and is used in the preparation of aniline dyes. The group of atoms $-CH_3$ which combines with the monovalent atom $-Cl$ to form methyl chloride is a monovalent group, the *methyl group*, a good example of an *organic radicle.*

39. *Methylene dichloride* CH_2Cl_2 has no special points of interest beyond the fact that the further substitution of chlorine for hydrogen causes the boiling point of the derivative to rise. Thus the boiling points of marsh gas, methyl chloride, and methylene dichloride are $-164°$, $-22°$, and $+42°$, respectively.

40. We get further evidence of the effect of substituting chlorine for hydrogen in the case of *chloroform*, $CHCl_3$ which is a volatile colourless mobile liquid of specific gravity 1·527, boiling at 61°. It dissolves fats and has a powerful anaesthetic effect.

Chloroform is prepared by the action of bleaching powder on alcohol.

Exp. 17.—Take a large flask and place in it about 100 grammes of bleaching powder made into a paste with water; add about 10 c.c. of alcohol. Fit to the flask a cork and tube leading to a condenser, and distil the mixture carefully (Fig. 8), or better, from a water bath. The resulting distillate separates into two layers of which the lower is chloroform. It may be identified by its smell and by the following reaction.

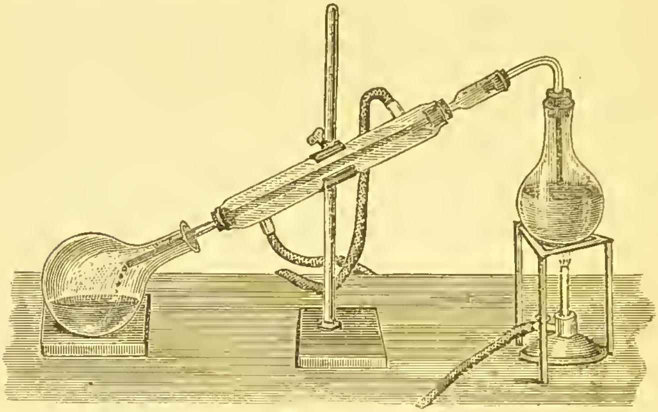


Fig. 8.

Exp. 18.—Heat a few drops of chloroform with aniline and caustic potash solution. A characteristic smell is noticed, the *iso-nitrile* smell, a test for chloroform.

The explanation of this mode of preparation of chloroform is in two stages, which will be much more easy to understand after a consideration of the properties of aldehydes, see § 66 and 67.

41. *Carbon tetrachloride*, CCl_4, is most readily prepared from carbon disulphide by passing chlorine through it. It is a colourless volatile mobile liquid with a smell similar to that of chloroform and with anaesthetic properties. It boils at 77°. It is interesting to note that it keeps up the gradation of properties of the haloid derivatives of the hydrocarbons though it contains no hydrogen at all.

42. Another important haloid derivative of marsh gas is obtained by the action of iodine and caustic potash on alcohol. The action is similar to that of chlorine and slaked lime on alcohol, which produces chloroform.

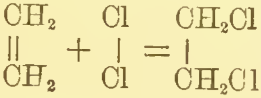
Exp. 19.—Put into a test tube some dilute alcohol and a few crystals of iodine. When the iodine has partly dissolved, add a few drops of a strong solution of caustic potash. The colour of the solution turns to yellow, a solid separates out, and a characteristic smell is noticed. The yellow solid is iodoform.

Iodoform, CHI_3 is a yellow solid which is soluble in alcohol but so insoluble in water that its formation is used as a test for alcohol. It melts at 119° and decomposes at a higher temperature with the liberation of iodine.

The explanation of its formation is similar to that of chloroform.

43. When ethylene and chlorine are brought together in equal volumes, they combine with the formation of a dichlor ethane, *ethylene dichloride*, $C_2H_4Cl_2$, which from its mode of formation must be $CH_2Cl - CH_2Cl$.

The equation representing its formation may be given



$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{c} Cl \\ | \\ Cl \end{array} = \begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

It is a colourless mobile liquid, boiling at 84°, and was first prepared in 1795.

Now when phosphorus pentachloride acts upon aldehyde, C_2H_4O, it substitutes two chlorine atoms for one oxygen atom, and gives a dichlorethane, $C_2H_4Cl_2$. This body boils at 57°, and is also formed by the action of chlorine on ethyl chloride, C_2H_5Cl. The explanation given is that in this case the two chlorine atoms are attached to the same carbon atom, while in the former case they are attached to different carbon atoms.

This body is called *ethylidene chloride*, and is represented by the formula $CH_3 - CHCl_2$.

The existence of these two bodies with the samo molocular formula, but with different properties is another illustration of *isomerism*, and of the extraordinary fertility of the hypothesis of valency applied to the question of molecular structure and structural formulae.

CHAPTER VI.

ALCOHOLS. ETHERS. GLYCERIN.

44. In inorganic chemistry we begin by considering the products of oxidation of common bodies, and we discover at once that there are elements and compounds, and that the elements form oxides with contrasting characters which we call basic and acid oxides.

If we pursue this method in organic chemistry we find that it does not lead to much result. By trying to oxidise the hydrocarbons we generally get only carbon dioxide and water, though under certain circumstances, *i.e.* an insufficient supply of air or oxygen, we obtain hydrocarbons with less hydrogen than the originals, *e.g.* acetylene from marsh gas.

45. On the other hand when we act on the hydrocarbons with chlorine we form substitution derivatives which resemble the chlorides of the elements, if we consider the organic radicles, methyl $-CH_3$ and ethyl $-C_2H_5$, respectively, as playing the part of elements. Thus

$$\begin{array}{r|l} CH_3 & Cl \\ K & Cl \end{array}$$

If we take this point of view we should expect to be able to obtain oxides or hydroxides of the radicles by the general method of preparing bases, *i.e.* by tho action of caustic potash on the salt. When this experiment is tried, that is when a solution of methyl chloride, or when methyl iodide is heated with caustic potash, in addition to the ethylene already noted, a liquid is formed which mixes with water but may be partly separated from it by distillation as it boils at 66°.

Analysis gives the formula CH_4O which agrees with the inference that the hydroxide CH_3OH should be formed, as suggested in the equation

$$CH_3Cl + KOH = CH_3OH + KCl$$

If this is confirmed we must consider the hydrocarbons as *hydrides* of the organic radicles of which we have now been able to prepare a chloride and a hydroxide in the case of methyl,

CH_3Cl = methyl chloride,
CH_3OH = methyl hydroxide,
CH_3H = methyl hydride,

so that we have been able to produce oxidation of our hydrocarbons, not directly, but by the stratagem of replacing hydrogen by chlorine and then chlorine by hydroxyl.

46. When prepared in this way the hydroxides are found to be identical with bodies prepared in many other ways, *e.g.* by the action of caustic potash on essential oils, the fermentation of sugary solutions, and the distillation of organic compounds.

Spirit of Wine or common *alcohol* is the most familiar of the class and may easily be investigated.

Exp. 20.—Take a large flask and place it in some solution of grape sugar. Place some yeast in the flask and shake it well; put the flask in a warm place and allow it to stand for a few days. Observe the frothing and prove that it is due to the formation of carbon dioxide. After a time, fit the flask with a cork and bent tube connected with a condenser (Fig. 8), and distil off a few c.c. of the liquid. Apply a light to a few drops; the liquid burns. Mix a few drops with water, iodine and caustic potash solution, the characteristic smell of iodoform is noticed.

By the action of yeast on grape sugar solutions alcohol is formed. Examine the yeast under a microscope and notice that it is composed of small rounded plant cells belonging to the class of the Fungi. This plant Saccharomyces (Torula) cerevisiae, as woll as several others, when immersed in water obtains part of the energy required for building up its cell substance from a splitting up of sugar into carbon dioxide and alcohol. The equation

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2$$

represents 95 per cent. of the changed sugar, about 3 per cent. appearing as glycerin, and ·5 per cent. as succinic acid. The other 1·5 per cent. is apparently oxidised further.

[It may be noted here that in presence of more oxygen than can be obtained from its solution in water, sugar is almost completely oxidised by yeast to carbon dioxide and water, so that in the manufacture of bread only a very small amount of alcohol is formed.]

The alcohol prepared by distillation is naturally wet, and it is dried by standing over and distillation from quicklime. This removes nearly all the water and the final traces are removed when required by sodium.

47. Pure or absolute alcohol is a colourless liquid with a characteristic burning taste and smell. It burns when lighted. It boils at 78·3°, freezes at −130°; and has a specific gravity of ·79. It mixes in all proportions with water and with ether, and it readily absorbs water vapour from the air. On mixing with water there is a contraction of volume, 52 c.c. of alcohol and 48 c.c. of water making only 96·4 c.c. of the mixture. Its solution in water will not light gunpowder moistened with it until it contains 49·3 per cent. by weight of spirit, thus forming *proof spirit.*

Chlorine acts upon alcohol, substituting three hydrogen atoms by three chlorine atoms and at the same time removing two more hydrogen atoms by oxidation. A body of the formula C_2Cl_3HO is formed, which is called *chloral* and which crystallises from water forming *chloral hydrate*, $C_2Cl_3H_3O_2$.

Hydrochloric and hydrobromic acids act on alcohol substituting chlorine or bromine for one oxygen and one hydrogen atom, and forming ethyl chloride and ethyl bromide, respectively. These reactions suggest the basic character of alcohol, thus

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O$$

Hydriodic acid also replaces hydroxyl by hydrogen, forming an iodide as an intermediate product, but the hydriodic acid attacks this iodide forming free iodine and ethane; this may be put in equation form, thus

$$\begin{cases} C_2H_5OH + HI = C_2H_5I + H_2O \\ C_2H_5I \quad + HI = C_2H_6 + I_2 \end{cases}$$

Sulphuric acid combines with alcohol, forming an acid sulphate, *hydrogen ethyl sulphate*, thus

$$C_2H_5OH + H_2SO_4 = C_2H_5 . HSO_4 + H_2O$$

Oxidising agents, *e.g.* chromic acid or alkaline permanganate solution oxidise alcohol very readily to *aldehyde.*

Exp. 21.—Take two or three drops of alcohol in a test tube and add potassium bichromate solution and sulphuric acid. Warm the mixture, the chromic acid turns green from reduction, and a new and characteristic fruity smell is noticed.

48. Since nitric acid is an oxidising agent as well as an acid, its reaction with alcohol is very complicated, part of the alcohol being oxidised and part of the nitric acid being reduced. The reduced nitrous acid combines with the alcohol to form *ethyl nitrite*, $C_2H_5NO_2$, as well as *ethyl nitrate*, $C_2H_5NO_3$. Ethyl nitrate can be formed in this reaction by removing the nitrous acid as fast as it is formed by some readily oxidisable body such as urea.

Exp. 22.—Take two test tubes; into both put a few drops of alcohol and nitric acid, but into one put some urea as well. Warm both of them. Both give off a pleasant smell, but the urea mixture does not give off as much nitrous fumes as the other.

Alcohol then has the properties of an ordinary base and combines with acids, forming salts and water.

Sodium dissolves readily in alcohol, replacing hydrogen and forming a body sodium alcoholate or *sodium ethylate*, represented by the formula C_2H_5ONa.

49. A most important reaction is that between alcohol and the haloid compounds of phosphorus. Phosphorus pentachloride acts readily on alcohol, substituting one chlorine atom for one oxygen and one hydrogen atom, and forming ordinary ethyl chloride, C_2H_5Cl. These two

atoms must hence be arranged in the molecule in the form of a group (— O — H), a *hydroxyl group*. The reaction is so characteristic that it is used in the preparation of the haloid derivatives of the paraffins. The phosphorus compound need not be made first, but can be formed during the progress of the reaction.

Exp. 23.—Into a flask put about 20 c.c. of alcohol (methylated spirit will do), and add to it three grammes of amorphous phosphorus. Weigh out as much iodine as would be required to combine with the phosphorus, to form phosphorus tri-iodide = about 30 grammes, and add it gradually to the alcohol until it is all dissolved. Allow the mixture to stand for some hours, adapt a condenser (Fig. 8), and then distil it. After shaking with dilute caustic potash solution, separate the heavy *ethyl iodide*, dry it by standing over dry calcium chloride and redistil (Fig. 3).

Alcohol dissolves many substances insoluble in water, *e.g.* resins, etc., and so is much used in manufactures. To avoid the consumption of this alcohol, which does not pay duty, it is *methylated* by adding 10 per cent. of crude wood spirit and as much paraffin as it will dissolve. On the Continent, bone oil is often added for the same purpose.

50. Before leaving the subject of alcohol it would be well to give an inductive proof of the structural formula of alcohol, based on the properties given above.

(i) The percentage composition and molecular weight indicate the formula C_2H_6O.

(ii) By the action of sodium upon alcohol one hydrogen atom is substituted by one sodium atom, and so one hydrogen atom must be different from the other five. We indicate it by writing the formula, thus

$$C_2H_5O - H'.$$

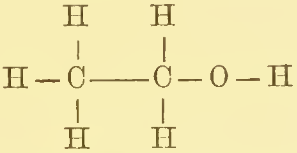
(iii) Phosphorus pentachloride removes one oxygen and one hydrogen atom and substitutes one chlorine atom. Hence we must assume that the oxygen and the hydrogen atom are arranged as a monovalent group, the hydroxyl group. Call the hydrogen atom of the hydroxyl group H″. Our formula now reads

$$C_2H_4\begin{matrix}.\,H'\\.\,OH''\end{matrix}$$

(iv) We have now to decide whether the hydrogen atom replaced by sodium is the same as that replaced with oxygen by phosphorus pentachloride, *i.e.* are H′ and H″ identical? We can try (i) the action of phosphorus pentachloride on the sodium substitution derivative, and (ii) the action of sodium on the chlorine derivative. In (i) the sodium atom disappears with oxygen, and their place is taken by chlorine, in (ii) the action of sodium gives us an entirely different body from the original, or the sodium derivative, viz., the hydrocarbon, *butane*, C_4H_{10}. Hence H′ and H″ must be identical and our formula now reads

$$C_2H_5\,.\,OH$$

This formula can only be arranged in one way to agree with the valencies of the atoms and the presence of the hydroxyl group, *i.e.*



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & —— & C & - O - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

which represents it as ethyl hydroxide. This is taken as the formula of alcohol.

We confirm this by building up alcohol from methane, by a series of steps making successively methyl chloride, ethane, ethyl chloride, and alcohol.

51. We may now return to the first alcohol made by the action of caustic potash solution on methyl chloride, *i.e. methyl alcohol.* This was first prepared and examined by Robert Boyle in 1661.

It is commonly prepared by the distillation of wood. The distillate, which is acid, is neutralised by lime and distilled. The fraction boiling about 60—70° contains the methyl alcohol. This wood spirit is very difficult to to purify. Methyl alcohol is also prepared by distilling

Wintergreen oil with caustic potash solution. Potassium salicylate is formed at the same time, see § 91.

$$\underset{\text{Wintergreen oil.}}{C_8H_8O_3} + KOH = \underset{\text{Potassium salicylate.}}{K . C_7H_5O_3} + CH_3OH.$$

Methyl alcohol is a colourless liquid boiling at 66° and of specific gravity ·8. Its properties are so similar to those of ethyl alcohol that it is not necessary to repeat them. It differs, however, when pure, in one important particular, viz. it does not form chloroform or iodoform by the reaction of bleaching powder or iodine and caustic potash solution respectively.

52. Some other alcohols are common bodies, *e.g.* fusel oil, $C_5H_{11}OH$, and it is possible to make many alcohols by general methods, *i.e.* from hydrocarbons, etc. (i) The most general method is the substitution of chlorine for hydrogen in the hydrocarbon, followed by the substitution of hydroxyl for chlorine by means of caustic potash, or better by freshly prepared silver hydroxide. This method gives a poor yield owing to the formation of ethylenes, and so a variation is generally used. (ii) The iodo derivative is warmed with sodium acetate, thus forming an acetate of the alcohol, and the organic salt is then heated with caustic soda solution. The reaction may be expressed by equations, using, for simplicity, methyl iodide and alcohol as an example:—

$$\begin{cases} CH_3I + NaC_2H_3O_2 = CH_3 . C_2H_3O_2 + NaI \\ CH_3 . C_2H_3O_2 + NaOH = Na . C_2H_3O_2 + CH_3OH \end{cases}$$

53. If we attempt to prepare a hydroxide or alcohol from benzene by the action of caustic potash on monochlorbenzene, we find that no action takes place. If, however, we take the product of the action of sulphuric acid on benzene, benzene sulphonic acid, $C_6H_5SO_3H$, and treat that with caustic potash, first in solution to form a potassium salt, potassium benzene sulphonate, $C_6H_5SO_3K$, and then by fusing the salt with caustic potash in a silver basin, we find that a change has taken place. The fused mass is soluble in water, and on addition of dilute acid deposits a liquid which sinks to the bottom and may be separated. The liquid has a characteristic smell of carbolic

acid, and blisters the skin. Its percentage composition and molecular weight are represented by the formula C_6H_6O, and it is called *phenol*. Phosphorus pentachloride reacts with it and substitutes hydroxyl by chlorine, so that its formula must be represented by C_6H_5OH.

The mode of formation may be represented by the equation

$$C_6H_5 . SO_3K + KOH = C_6H_5OH + K_2SO_3$$

It is general for benzene compounds, and applies to the insertion of any number of hydroxyl groups.

54. Phenol is generally prepared from coal tar. The fraction of the distillate boiling between 150°—200° is taken, mixed with a solution of caustic soda and the heavy solution separated off. The solution is mixed with dilute sulphuric acid and the resulting oily liquid redistilled. The portion boiling about 180—190° is again separated and is phenol, or carbolic acid, so called because it combines with alkalies to form soluble compounds resembling salts. Phenol is generally liquid, but when freed from water may be crystallised as a solid melting at 42° and boiling at 182°. It is colourless when first prepared, but soon reddens on exposure to the air. It dissolves in fifteen parts of water, in alcohol and in ether.

Exp. 24.—To a solution of phenol in water add some ferric chloride solution to which alkali has been added until nearly neutral. A violet colour is seen. To some more of the solution add a drop of bromine. A yellowish precipitate is at once formed. Dip a pine splinter into phenol and then dip it into hydrochloric acid, it soon turns green. Add a solution of caustic potash to some phenol, it now dissolves in water.

Phenol has the characteristic reactions of benzene with sulphuric and nitric acids, forming *phenol sulphonic acid*, $C_6H_4\genfrac{}{}{0pt}{}{OH}{SO_3H}$, and *nitro phenol*, $C_6H_4\genfrac{}{}{0pt}{}{OH}{NO_2}$, respectively. A characteristic property of phenol is that it acts as a germicide in strong solutions, and better in the liquid state; in dilute solution, on the other hand, it has very little action.

[Another general method of preparing phenol is to pass from benzene through nitro-benzene and aniline. The latter is decomposed by boiling with nitrous acid forming phenol and nitrogen. See § 114.]

55. Since the properties of alcohols are similar to those of metallic bases we might expect that they would form oxides on heating, just as most bases do; but this is seldom the case, so that the alcohols resemble the caustic alkalies in this respect. It is, however, easy to remove water in presence of a dehydrating agent,—in the case of ethyl alcohol, sulphuric acid is used.

Exp. 25.—Fit up a flask with a condenser, dropping funnel and thermometer, reaching nearly to the bottom of the flask. In the flask place a mixture of about equal volumes of sulphuric acid and alcohol, and heat it by a sand bath to about 140°. Fill the dropping tube with a mixture of alcohol and sulphuric acid and allow it to trickle in from time to time. A volatile liquid comes over, with a characteristic smell of ether.

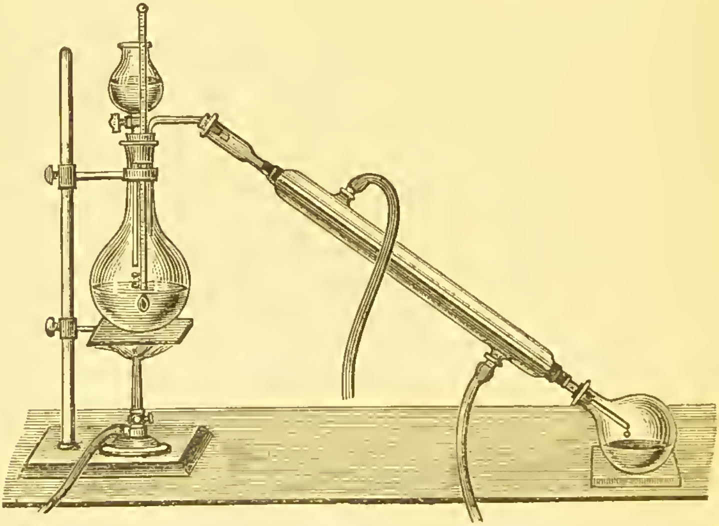


Fig. 9.

56. Ether is a volatile, mobile, colourless liquid of specific gravity ·72, boiling at 35° and solidifying at —129°. Its percentage composition and molecula weight are represented by the formula $C_4H_{10}O$. When rapidly volatilised the heat which is rendered latent in the ether vapour is supplied by any bodies with which it is in contact and they become very cold, so much so that an ether spray is largely used to produce local cooling.

Exp. 26.—Take a small beaker and place it on a few drops of water on a block of wood. Put some ether in the beaker and blow air through it by means of a tube and bellows. The ether cools, the water freezes, and the beaker sticks to the wood.

Ether acts as a solvent and is able to extract many bodies from their solutions in water. It has also a valuable anaesthetic action. Ether burns in air and explodes with oxygen; care must always be taken to evaporate ether only on a water bath and without a flame very near it.

Chlorine acts rapidly on ether, substituting chlorine for hydrogen atoms until finally it replaces them all forming $C_4Cl_{10}O$. This suggests that all the hydrogen atoms are similar, and so no hydroxyl group can be present. Hydrochloric acid has little action on ether. Hydriodic and sulphuric acids act upon ether, splitting it up into a mixture of ethyl alcohol and ethyl iodide or ethyl hydrogen sulphate, respectively.

Nitric acid and other oxidising agents oxidise ether.

Sodium and alkalies have no action on ether.

Phosphorus pentachloride acts upon ether when they are heated together, substituting two chlorine atoms for one oxygen atom and splitting it up at the same time into ethyl chloride. In order to explain this reaction we must assume that ether is an oxide of ethyl, $(C_2H_5)_2O$, corresponding to the hydroxide alcohol, C_2H_5OH, and bearing the same relation to it as the oxide of sodium, Na_2O, does to its hydroxide, $NaOH$.

57. We can now explain the reactions between sulphuric acid and alcohol. When sulphuric acid is mixed with alcohol, the acid sulphate, ethyl hydrogen sulphate, $C_2H_5 . HSO_4$, is formed, and the water is removed by the acid,

$$C_2H_5OH + H_2SO_4 = C_2H_5 . HSO_4 + H_2O.$$

The acid sulphate when heated to 160° in presence of sulphuric acid splits up into ethylene and sulphuric acid, thus:—

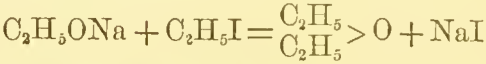
$$C_2H_5 . HSO_4 = C_2H_4 + H_2SO_4$$

But if there is an excess of alcohol and the temperature is kept below this, about 140°, then the alcohol reacts with the acid sulphate, forming ether and sulphuric acid. The equation may be given thus:—

$$C_2H_5 . HSO_4 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4$$

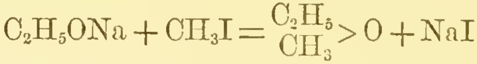
Since the sulphuric acid is regenerated, the process is continuous so long as the sulphuric acid is strong enough to form the acid sulphate. It is hence called the *continuous etherification process.*

Again, since hydriodic acid splits ether into alcohol and iodide, perhaps the process can be reversed to form ether. The reversal is at once brought about by acting on the alcohol first with sodium and then on the sodium derivative by the iodide. An equation may be given



$$C_2H_5ONa + C_2H_5I = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix} > O + NaI$$

This is a general reaction and is used to make *mixed ethers, e.g.* the action of methyl iodide on sodium alcohol would form *methyl ethyl oxide,*



$$C_2H_5ONa + CH_3I = \begin{matrix} C_2H_5 \\ CH_3 \end{matrix} > O + NaI$$

58. It may have been noticed that the formula $C_4H_{10}O$ could also be written to represent an alcohol, C_4H_9OH, *butyl alcohol* as well as ethyl ether, $(C_2H_5)_2O$. It would appear from this that the ethers have the same percentage composition and molecular weight as alcohols, *i.e.* they are isomeric compounds, but there is sometimes held to be a difference between isomerism of this kind and that which we have noticed between different hydrocarbons with the

same molecular formula, since these classes of compounds, the alcohols and ethers, have different class properties, while the hydrocarbons of the same formula have in general similar class properties. This variety of isomerism may be called *metamerism*, and the compounds *metamers*.

59. We have seen that the alcohols are hydroxides with oxides corresponding to them, they are *monacid* or *monad bases* derived from hydrocarbon radicles. We should therefore naturally expect to find diacid or diad bases and triacid or triad bases among the alcohols. This is the case, provided the hydroxyl groups are attached to different carbon atoms of the molecule, the case in which the hydroxyl groups are attached to the same carbon atom is considered in the next chapter.

[It must be mentioned that there is some confusion of terms about this point, and the terms monatomic, diatomic, etc., and monohydric, dihydric, etc., alcohols are sometimes used instead of the *base* terminology given above. A little consideration will shew the inadvisability of using the same adjective to express the number of atoms in a molecule and the number of hydroxyl groups in an alcoholic molecule.]

60. Only one of the polyad bases need be discussed now, viz. *glycerin* or *glycerol*, discovered by Scheele in 1779.

In the manufacture of soap by the action of caustic soda on fats, the watery solution left after the separation of the soap may be evaporated down and distilled. After the water has evaporated, a sweetish liquid is left, which boils at about 290°. Its molecular composition is represented by $C_3H_8O_3$, and it is *glycerin*. Glycerin is prepared now by the action of superheated steam on fats. Glycerin is a thick colourless syrup of specific gravity 1·27. It melts at 20° after being crystallised, and boils when pure at 290°. It is very hygroscopic and is used in the manufacture of stamping inks, flexible glue, etc.

Exp. 27.—Apply a light to a little glycerin on a crucible lid, it does not burn. Heat the glycerin to 150°. It now burns when lighted.

The reactions of glycerin are very complex. Chlorine causes oxidation. Hydrochloric acid forms salts, replacing one or two hydroxyl groups by chlorine. Sulphuric acid forms a sulphate of glycerin, and nitric acid a nitrate, which contains three nitrate groups and is a tri-nitrate, $C_3H_5(NO_3)_3$. This body is nitro-glycerin or *trinitrin*, which explodes violently when its detonation is once started by a shock. Phosphorus pentachloride removes three hydroxyl groups and replaces them by three chlorine atoms, forming trichlor propane, $C_3H_5Cl_3$. These facts are best explained on the assumption that the three carbon atoms are directly united, and that there are three hydroxyl groups, one united with each carbon atom thus

$$CH_2(OH) - CH(OH) - CH_2(OH).$$

This formula is confirmed by synthesis.

As glycerin is an alcohol we might expect changes on dehydration, thus distillation with calcium chloride removes three molecules of water from two molecules of glycerin, forming *glycerin ether*, $(C_3H_5)_2O_3$. Phosphoric anhydride or sodium hydrogen sulphate also remove water, forming *acroléin*, C_3H_4O, a body with a characteristic smell of burnt fat.

CHAPTER VII.

ALDEHYDE. CHLORAL. SUGARS.

61. As the oxidation of the hydrocarbons by the introduction of hydroxyl for hydrogen has led to a distinct class of bodies, the alcohols, and as alcohol so readily reduces common oxidising agents, it would be well to investigate the oxidation products of alcohol more carefully.

Exp. 28.—Take a flask fitted with a thistle funnel, and connected with a condenser, and place in it 20 grammes of potassium bichromate covered by 60 c.c. of water.

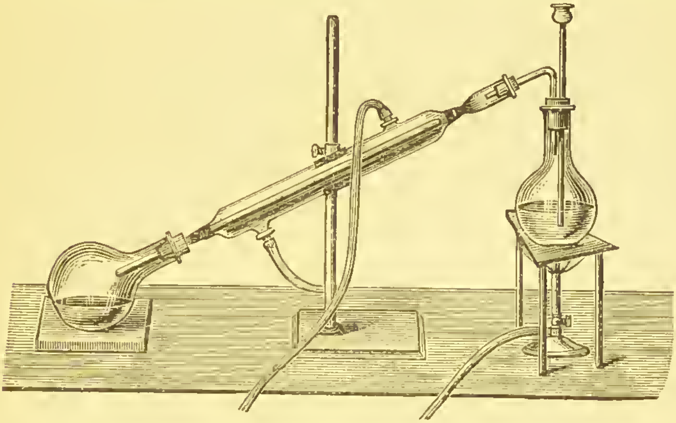


Fig. 10.

Drop in a cold mixture of 20 c.c. of alcohol and 15 c.c. of strong sulphuric acid. Be careful not to allow the temperature to rise, and not to run in the alcohol mixture too quickly. Redistil the distillate from a water bath at a temperature of 30°, using a good condenser, and collect the portion boiling about 20—22°.

The distillate has different properties from alcohol, and its composition and molecular weight are represented by the formula C_2H_4O. Since its formula differs from that of the parent alcohol, C_2H_6O, by two hydrogen atoms it is called *ethyl* or *acetic aldehyde*, or more shortly, *aldehyde*.

62. Aldehyde is a colourless mobile liquid with a characteristic fruity smell and burning taste. It boils at 21°. It is soluble in water, alcohol and ether, and readily dissolves sulphur, phosphorus, iodine and resins. Chlorine acts upon aldehyde forming various compounds: in presence of chalk and water it substitutes three chlorine atoms for three hydrogen atoms, and forms *chloral*, C_2HCl_3O, thus suggesting that three of the hydrogen atoms are similarly situated to each other and differently from the other one. Hydrochloric and sulphuric acids cause a curious and characteristic change. At ordinary temperatures the effect of these acids is to raise the boiling point of the liquid, and at the same time its molecular weight becomes tripled. It is now represented by the formula $(C_2H_4O)_3$ as a polymer of aldehyde, and it is called *paraldehyde*. If the aldehyde is at 0° the acids cause it to polymerise into a solid, *metaldehyde*.

Nitric acid, chromic acid and other oxidising agents are readily reduced by aldehyde, more readily than by alcohol.

Exp. 29.—Take a solution of silver nitrate in a test tube, add to it a few drops of ammonia solution until the precipitate at first formed redissolves. Then add a few drops of potash solution until the solution becomes slightly turbid. Add a few drops of aldehyde. The silver is reduced, more quickly on warming, in the form of a lustrous metallic lining to the tube, the *silver mirror*.

Add a few drops of aldehyde to some Fehling's solution of copper and boil. The yellow precipitate of reduced cuprous oxide is seen.

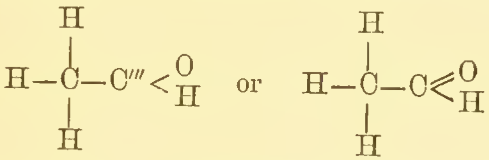
This reduction of silver and copper is used as a test for aldehyde.

Sodium amalgam reduces aldehyde again to alcohol.

In presence of caustic alkalies aldehyde is readily resinified to *aldehyde resin*, another characteristic test.

Exp. 30.—Boil a few drops of aldehyde in a test tube with a strong solution of caustic potash. It turns yellow and then brown from the formation of aldehyde resin.

63. Phosphorus pentachloride substitutes two chlorine atoms for one oxygen atom, indicating the absence of any single hydroxyl group, and also that the carbon atoms are not joined by the oxygen atom. Hence if three hydrogen atoms are similarly situated (see § 62), if there is no hydroxyl group and if the carbon atoms are connected, we arrange the formula for aldehyde thus :—



$$\mathrm{H}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\mathrm{C}'''<^{\mathrm{O}}_{\mathrm{H}} \quad \text{or} \quad \mathrm{H}-\overset{\displaystyle\mathrm{H}}{\underset{\displaystyle\mathrm{H}}{\mathrm{C}}}-\mathrm{C}\lll^{\mathrm{O}}_{\mathrm{H}}$$

The first formula assumes that the valency of an atom is determined in every case by the number of other atoms on which it is acting directly; in this case carbon is trivalent and oxygen monovalent. The second or double bond form assumes that carbon is always tetravalent and oxygen divalent.

These formulae do not readily indicate the connection between aldehyde and alcohol; the properties of chloral, together with the compounds formed by oxidising alcohol with potassium permanganate, suggest the most probable explanation of the formula of aldehyde and of its properties. Probably oxidation of alcohol to aldehyde takes place in a usual manner, viz. the oxidation of a hydrogen atom to a hydroxyl group, which may be represented thus :

$$2\,CH_3CH_2OH + O_2 = 2\,CH_3CH(OH)_2$$

Under ordinary circumstances two hydroxyl groups attached to the same carbon atom readily split off water, in this case $CH_3CH(OH)_2 = CH_3CHO + H_2O$

We have evidence of a similar property of metallic bases in the cases of mercuric hydroxide which has not been prepared, as it immediately splits up into mercuric oxide and water, and cupric hydroxide, which splits off water when warmed.

We can now understand why phosphorus pentachloride substitutes the oxygen atom by two chlorine atoms, since the oxygen atom represents two hydroxyl groups.

64. Aldehyde with its two hydroxyl groups has the properties of a metallic peroxide, and can unite both with a weak acid and a weak base; thus it combines (i) with ammonia forming a clear crystalline compound, *aldehyde ammonia*, and (ii) with hydrocyanic acid forming a hydroxy cyanide. Equations may be given,

(i) $CH_3CH(OH)_2 + NH_3 = CH_3CH(OH)NH_2 + H_2O$
(ii) $CH_3CH(OH)_2 + HCN = CH_3CH(OH)CN + H_2O$

65. Starting with methyl alcohol instead of ethyl, it is oxidised in the same way to the aldehyde of the lowest possible carbon content, *formaldehyde* or *methyl aldehyde*, represented by the formulae

$$H - CHO \quad \text{or} \quad HCH(OH)_2$$

This body is readily formed by the oxidation of methyl alcohol by free oxygen under the influence of platinum, but its special interest is connected with the probability that it is the first product of reduction of carbonic acid by the green plant, which may perhaps be represented by the equation

$$CO(OH)_2 + H_2O = HCH(OH)_2 + O_2$$

Its properties are similar to those of aldehyde.

66. *Chloral* is prepared by passing chlorine through alcohol for a long time. The resulting liquid is distilled, mixed with water, and choral hydrate, CCl_3CHO, H_2O or $CCl_3CH(OH)_2$, is crystallised out.

Chloral hydrate is a colourless crystalline solid with a faint smell, which is more pungent on warming. It dissolves in water, and is readily acted on by caustic alkalies with separation of chloroform.

Exp. 31.—Take a few crystals of chloral hydrate and dissolve them in water in a test tube. Add caustic potash, the solution turns milky and drops are soon noticed with the characteristic smell of chloroform.

We find out what has taken place when we discover that the solution contains another compound, potassium formate, HCO_2K, so that the reaction may conveniently be expressed in equation form, thus:

$$CCl_3CH(OH)_2 + KOH = CHCl_3 + HCO_2K + H_2O$$

67. The formation of chloroform by the action of bleaching powder on alcohol may also be simply but not completely explained. (*a*) The hypochlorite oxidises the alcohol to aldehyde and at the same time chlorinates it in presence of free lime by substituting three chlorine for three hydrogen atoms, forming chloral. (*b*) The alkali, lime acts upon the chloral formed and splits it into chloroform and calcium formate. An exactly similar explanation may be given for the formation of iodoform, the intermediate product being *iodal*, CI_3CHO.

68. A very large number of interesting scents and flavours, *e.g.* oil of bitter almonds, vanilla, etc., are derived from aldehydes, but these are generally beyond the scope of this work. There is, however, another class of bodies which have characteristic aldehyde reactions. These are sweet bodies which crystallise out of plant or fruit juices and are called sugars. Other sugars are also obtained from animals, notably the sugar contained in milk and prepared by the evaporation of whey.

Now though it has not been possible to convert the sugars into vapour without decomposing them, their molecular weights have been determined by other methods. We should first, therefore, examine their percentage composition:

	Grape Sugar.	Cane Sugar.
Carbon	40·00	42·11
Hydrogen	6·67	6·43
Oxygen	53·33 = 8 × 6·67	51·46 = 8 × 6·43
	100·00	100·00

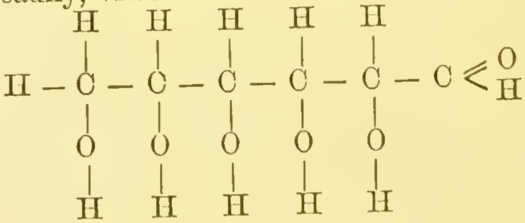
Though the sugars have not all the same composition, yet they agree in having the ratio of oxygen to hydrogen as eight to one, exactly the same ratio as these elements have in water. The composition of grape sugar is apparently the simplest, being represented by CH_2O, or some multiple of it, cane sugar being represented by $C_{12}H_{22}O_{11}$. The multiple in the case of grape sugar, as determined by solution methods of determining molecular weights, is 6, so that grape sugar is $(CH_2O)_6$ or $C_6H_{12}O_6$. Nearly all the sugars of higher molecular weight, when boiled with dilute acids, are changed to bodies of the same percentage composition as grape sugar and with similar properties.

69. *Grape sugar*, dextrose, or glucose is found in most ripe sweet fruits and may be crystallised from their juice. It is found crystallised in raisins. It is a crystalline solid melting when pure at 86°. Hydrochloric acid acts on it, substituting chlorine for hydroxyl and forming chlorides. Nitric acid has a similar action, forming nitrates, so that grape sugar is basic, *i.e.* probably alcoholic in character. It dissolves in sulphuric acid, but is not readily charred by it. Grape sugar is oxidised by chromic acid, a property of an alcohol though it is also characteristic of an aldehyde.

> **Exp. 32.**—Boil a little grape sugar solution with ammoniacal silver solution, Fehling's solution, and caustic potash solution. The first two are reduced, the last is turned brown.

Hence grape sugar reduces silver salts to the metal, cupric salts to cuprous, and is resinified by caustic potash, so that it has the characteristic properties of an aldehyde. It is also reduced to an alcohol by sodium amalgam.

Hence, on the whole, the best formula to sum up the properties of grape sugar should represent its carbon atoms as all connected, and as arranged to form an aldehyde and some alcohol groups. There is only one way of doing this readily, viz. :—



$$\begin{array}{ccccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C}{<}^{\mathrm{O}}_{\mathrm{H}} \\ & & | & & | & & | & & | & & | & & \\ & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \mathrm{O} & & \\ & & | & & | & & | & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

or in the abbreviated form $CH_2OH(CHOH)_4CHO$.

Grape sugar has a characteristic property in being fermentable by yeast into alcohol and carbon dioxide; it also rotates the plane of polarisation of light.

70. *Cane sugar* is obtained from the juice of the sugar cane, or beet root. The juice is either expressed and evaporated in vacuum pans, or diffused out into water and then evaporated. It is purified by being passed in solution through animal charcoal and then crystallised out.

Cane sugar has a characteristic sweet taste and dissolves in one-third of its weight of water.

Exp. 33.—(*a*) Boil some cane sugar solution with potash solution and Fehling's solution. Then boil some more cane sugar with dilute sulphuric acid for some time, say half-an-hour, and try these tests again.

(*b*) Pour some strong sulphuric acid on cane sugar.

It does not reduce Fehling's solution until after being boiled for some time. It is blackened by strong sulphuric acid. It is changed by boiling with dilute sulphuric acid for a short time, and now gives the grape sugar tests at once.

Analysis shews that it is split up by dilute acids into a mixture of equal parts of grape sugar and another sugar of the same percentage composition and molecular weight, called *laevulose*. Laevulose is isomeric with dextrose. This reaction may be represented by an equation

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{dextrose.}}{C_6H_{12}O_6} + \underset{\text{laevulose.}}{C_6H_{12}O_6}$$

This kind of chemical change or splitting, produced simply by the addition of water, is called *hydrolysis.*

Grape and cane sugars are typical of two most important classes of the *carbohydrates*, so called because of the relationship of oxygen to hydrogen in their percentage composition. It must not be assumed however, that they are *water compounds.*

CHAPTER VIII.

ACIDS.

71. HAVING observed that aldehydes possess reducing properties, it becomes advisable to examine the products of their oxidation, and in order to do so we submit the aldehyde or alcohol to the action of the oxidising agent for some time.

Exp. 34.—Take a half-litre flask, fitted with a cork and upright condenser so as to run the distillate back. Place in the flask about twenty grammes of potassium bichromate covered with dilute sulphuric acid (one in five). Warm by a water-bath and pour down the condenser a few c.c. of aldehyde or alcohol. The smell gradually changes to that of vinegar. Turn the condenser down and heat the flask. Collect the distillate coming over from 110° to 120°. Test it with litmus, chalk, etc. It it acid.

The acid distillate appears to be similar to vinegar, and to wood vinegar, from which it is generally prepared.

72. Vinegar is prepared from dilute spirit solutions, by the action of Bacterium aceti, a Fungus which oxidises the alcohol by means of the oxygen of the air while the solution is trickling over faggots.

The watery liquid obtained in the dry distillation of wood contains wood spirit, and is also sour from the presence of an acid.

From both of these products a pure acid is prepared by neutralisation with lime and crystallisation of the lime salt. The lime salt is purified by recrystallisation and distilled with hydrochloric or sulphuric acid. The acid distils over.

Exp. 35.—Take a small retort, place in it about five or ten grammes of calcium or sodium acetate. Cover it with strong sulphuric acid. Heat carefully and collect the product. It is a pungent smelling liquid. Test it with litmus.

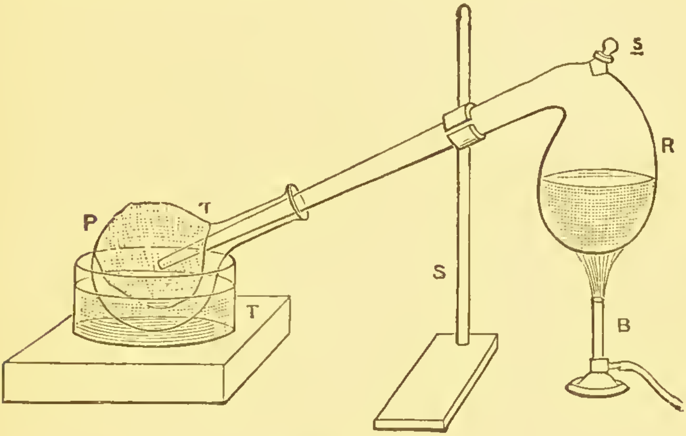


Fig. 11.

Whether prepared from aldehyde or vinegar, the properties of the body are the same. Its percentage composition and molecular weight are represented by the formula $C_2H_4O_2$, and it is called *acetic acid.*

73. Pure acetic acid is a colourless liquid of specific gravity 1·055. It blisters the skin, and has a characteristic pungent smell, which on dilution is like that of vinegar. It melts at 17° and boils at 118°. The vapour density of its vapour has the peculiarity of being nearly twice as great just above the boiling point as at higher temperatures; it has been supposed that it has a higher molecular weight at low temperatures than at high ones. Each molecule at the lower temperature may perhaps be represented by $(C_2H_4O_2)_2$. It acts as a solvent for many bodies which are insoluble in water, *e.g.* sulphur and phosphorus.

Exp. 36.—Apply a light to some acetic acid in a basin. It does not burn. Heat the basin and apply a light to the boiling acid; its vapour now burns.

Chlorine acts upon acetic acid by substitution only, and substitutes three chlorine for three hydrogen atoms in succession, producing three different compounds, monochloracetic, dichloracetic, and trichloracetic acids. No oxidation is noticed.

Hydrochloric acid, sulphuric acid, nitric acid, chromic acid, and oxidising agents generally have no action on acetic acid, but an alkaline solution of potassium permanganate is able to oxidise it (to oxalic acid). Phosphorus pentachloride acts on acetic acid, substituting one chlorine atom for hydroxyl, and forming *acetyl chloride*, $C_2H_3O \, . \, Cl$, a fuming liquid.

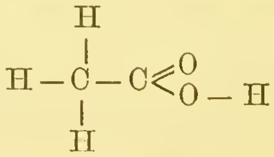
74. The most characteristic compounds of acetic acid are its salts, prepared by the direct reaction between the acid and bases or basic oxides. Acetic acid is a monobasic acid and only contains one atom of replaceable hydrogen per molecule. All its salts are soluble in water, but they are frequently decomposed by boiling water and give precipitates of a basic salt.

Exp. 37.—Neutralise some acetic acid with soda and crystallise out the sodium acetate.

Dissolve litharge or lead carbonate in moderately strong acetic acid and crystallise out lead acetate (sugar of lead).

Add a solution of acetate of soda to ferric chloride. A red solution of ferric acetate $Fe(C_2H_3O_2)_3$ is seen. Neutralise and boil this, and a brown precipitate of basic ferric acetate comes down $Fe(OH)_2C_2H_3O_2$. This precipitate is insoluble in water and is used to remove iron from solutions containing phosphates.

75. We have now sufficient data to decide on the formula of acetic acid, and we arrange it thus:



$$\begin{array}{ccccl} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C}\begin{array}{l}\lt \mathrm{O} \\ \lt \mathrm{O}-\mathrm{H}\end{array} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

This formula embodies the facts:

(*a*) One atom of hydrogen is replaceable by metals and one hydroxyl group by chlorine under the action of phosphorus pentachloride.

(*b*) Three hydrogen atoms are different from the other one and can be substituted by chlorine without destroying the acid characters of the body.

(*c*) It is prepared from aldehyde by oxidation, one hydrogen atom being oxidised into a hydroxyl group. Thus:

$$2\,CH_3CHO + O_2 = 2\,CH_3COOH$$

76. It would perhaps be well to write out an inductive proof of the formula in sequence, thus:

(*a*) The percentage composition of acetic acid is represented by the formula CH_2O.

(*b*) The molecular weight is 60, so the molecular composition is represented by $2\,(CH_2O)$ or $C_2H_4O_2$.

(*c*) Metals, basic oxides and bases act on acetic acid replacing one atom of hydrogen by one atom of the metal of a monad base, so we can write the formula of the body.

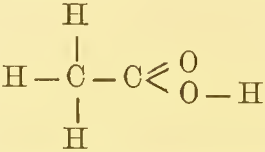
$$C_2H_3O_2\,.\,H$$

(*d*) Phosphorus pentachloride acts on acetic acid, replacing one oxygen and one hydrogen atom by one chlorine atom, forming C_2H_3OCl. Hence we assume that a hydroxyl group is present, and may write the formula $C_2H_2O\,.\,\substack{H \\ OH}$. Now in order to decide whether the hydrogen atom replaced by metals is the same as that of the hydroxyl group, we endeavour to act upon the chloride by caustic soda. This only substitutes sodium again in place of the chlorine by adding oxygen as well so that we can assume that these two hydrogen atoms are the same and write the formula

$$C_2H_3O\,.\,OH$$

(*e*) The action of chlorine in replacing one, two or three hydrogen atoms by the same number of chlorine atoms without altering the basicity and general properties of the acid confirms the fact that three hydrogen atoms are differently situated from the other one.

(*f*) Considering these facts in the light of the valencies of the atoms concerned, the formula must be arranged like this:



$$\begin{matrix} & & H & & \\ & & | & & \\ H & - & C & - & C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown O-H\end{smallmatrix} \\ & & | & & \\ & & H & & \end{matrix}$$

and it agrees with the fact of the formation of acetic acid by oxidation.

77. The process of oxidation is evidently only a continuation of the oxidation of alcohol to aldehyde by the conversion of a hydrogen atom into a hydroxyl group, thus alcohol, CH_3CH_2OH is oxidised to aldehyde, $CH_3CH(OH)_2$, which is oxidised further to acetic acid $CH_3C(OH)_3$. Just as aldehyde cannot keep its two hydroxyl groups attached to one carbon atom, so acetic acid cannot do so and water is split off, leaving $CH_3 - C\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown OH\end{smallmatrix}$ This monovalent group of atoms ($-COOH$) is termed the *carboxyl group*, and is characteristic of organic acids. So general is the presence of this group in organic acids that it has been adopted to define them in preference to the properties selected for defining inorganic acids.

78. [Additional weight is given to the formula for acetic acid by another method of building it up, from marsh gas.

Methyl chloride or iodide is converted into methyl cyanide by the action of an alcoholic solution of potassium cyanide. The resulting methyl cyanide contains two atoms of carbon, so we have added one carbon atom to the methyl group. When the cyanide is boiled with dilute acids it splits up into ammonia which combines with the acid, and acetic acid, thus:

$$\begin{aligned} CH_3CN + 3\,H_2O + HCl &= CH_3C(OH)_3 + NH_4Cl \\ &= CH_3COOH + NH_4Cl + H_2O \end{aligned}$$

This is a most important general method of synthesising organic acids by the addition of carbon atoms, one at a time].

79. When we start to oxidise methyl alcohol, HCH_2OH, or methyl aldehyde, $HCHO$, we prepare at once an acid with the molecular composition represented by the formula, $HCOOH$, and called *formic acid*, from its identity with an acid first prepared by distilling red ants. The method of preparing acids by oxidising alcohols is thus a general method.

Formic acid is also prepared by distilling oxalic acid with glycerin, but the reaction is complicated.

Formic acid is a colourless liquid of specific gravity 1·22, boiling at 99·9° and freezing at 8·6°.

Its reactions are very similar to those of acetic acid, and all its salts are soluble. As it has only one carbon atom it is the lowest acid and cannot very readily form substitution derivatives.

80. It has, however, two very important differences from acetic acid. (*a*) When boiled with sulphuric acid it forms carbon monoxide. (*b*) It is very readily oxidised even by weak oxidising agents.

Exp. 38. Take a test tube and pour into it about 1 c.c. of formic acid and 5 or 10 c.c. of sulphuric acid and heat. Apply a light to the mouth of the tube. The gas given off burns with a characteristic blue flame forming carbon dioxide, so that it is carbon monoxide.

Take a solution of silver nitrate, add to it ammonia and potash, as in Exp. 30, and add formic acid and warm. A silver mirror forms. Take a solution of mercuric chloride, and add formic acid and boil. The mercuric chloride is reduced to mercurous chloride.

This difference between the two acids is best explained after an inspection of the formula $HCOOH$, which can be arranged in two ways: (i) as an acid $HCOOH$ or $\mathrm{H} \,\vdots\, \underbrace{\mathrm{C} \lessdot {}^{\mathrm{O}}_{\mathrm{OH}}}_{\text{Carboxyl Group.}}$ and (ii) as an aldehyde $HO - CHO$ or $\mathrm{H - O} \,\vdots\, \underbrace{\mathrm{C} \lessdot {}^{\mathrm{O}}_{\mathrm{H}}}_{\text{Aldehyde Group.}}$. In the latter case the formula is written as an aldehyde of hydroxyl which oxidises very readily to carbonic acid.

81. One important reaction of the acids has been already given. When heated with excess of sodalime the carboxyl group splits up, part being retained by the hydrocarbon formed from the residue of the acid, and part by the base in the form of carbonate. We can express the reaction generally by an equation using the symbol C_nH_{2n+2} to represent a paraffin.

$$C_nH_{2n+1}COONa + NaOH = C_nH_{2n+2} + Na_2CO_2$$

When sodium formate is heated with sodalime, $n = 0$, and hydrogen is formed.

[Two other important reactions may be noted. (i) Heating the calcium salt of the acid alone. (ii) Heating the calcium salt of the acid with calcium formate. The first reaction results in the formation of a derivative of the acid in which a hydrocarbon radicle takes the place of the hydroxyl in the carboxyl group, and which is termed a *ketone*. In the case of calcium acetate an equation which represents part of the reaction, viz. the formation of the ketone, *acetone*, is

$$\underset{\text{calcium acetate.}}{(CH_3COO)_2Ca} = \underset{\text{acetone.}}{CH_3COCH_3} + CaCO_3$$

When calcium formate is used the hydrogen of the formate enters the carboxyl group in place of the hydroxyl group, thus causing a reduction of the acid to aldehyde. We may represent this part of the reaction, in the case of heating calcium acetate and formate, by an equation,

$$\underset{\text{calcium acetate.}}{(CH_3COO)_2Ca} + \underset{\text{calcium formate.}}{(HCOO)_2Ca} = \underset{\text{aldehyde.}}{2\,CH_3CHO} + 2\,CaCO_3$$

The second reaction is of great interest, as it enables us to prepare aldehydes direct from acids containing the same number of carbon atoms.]

82. Many aromatic resins when heated with lime yield benzene, and when gum benzöin is heated by itself it forms a nearly colourless sublimate of fine needle-shaped crystals. These crystals when heated with lime yield

benzene and calcium carbonate, so that they are a source of benzene. On analysis the crystals are found to have the molecular formula $C_7H_6O_2$. They melt at 121° and boil at 250°. They are much more soluble in hot water than in cold; they dissolve readily in alkalies, and may be crystallised out from their solutions, in the form of salts which are much more soluble in water than the original substance.

When treated with phosphorus pentachloride, hydroxyl is replaced by chlorine forming a characteristic compound, resembling acetyl chloride. These reactions can be best explained by assuming that the crystals are an acid, *benzoic acid*, and that it contains the benzene ring, thus:

$$C_6H_5COOH$$

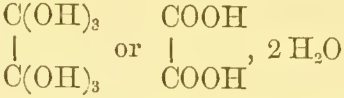
Confirmation is obtained (i) by the formation of the acid from toluene, $C_6H_5CH_3$ by the action of chromic acid, and (ii) by its synthesis from benzene by passing form benzene to benzene cyanide or *benzonitrile*, C_6H_5CN (see § 108), followed by the splitting of this compound under the action of dilute acids or alkalies to form benzoic acid, C_6H_5COOH, and ammonia.

83. When sorrel or rhubarb juice is evaporated a crystalline salt is formed, which is decomposed on heating, leaving potassium carbonate behind, and forming carbon monoxide and carbon dioxide. This suggests the presence of a salt of potassium with an organic acid, so we must try to prepare the acid in the usual way, by precipitating the potassium salt as a lead salt by the addition of lead acetate, and precipitating the lead as lead sulphide by sulphuretted hydrogen.

Exp. 39. Dissolve 10 or 15 grammes of salt of sorrel in water. Add a solution of lead acetate. Filter the precipitate and wash it well. Suspend the precipitate in water and pass in sulphuretted hydrogen. When all the lead is precipitated as lead sulphide, filter, and evaporate the filtrate, crystals separate out.

The crystals have the composition represented by the formula CH_3O_3, and are called *oxalic acid*, but as water is given off on heating and the substance left has much the same properties as the acid, the formula might be written CO_2H, H_2O. This substance is an acid, turning litmus red, and forming salts and water when reacting with basic oxides and bases.

By solution methods we find its molecular weight is represented by the double formula $C_2H_6O_6$ or $C_2H_2O_4$, $2\,H_2O$, so that we can now make use of the fact that it has the same formula as carboxyl, a monovalent group, by writing the formula thus:



$$\begin{array}{c} C(OH)_3 \\ | \\ C(OH)_3 \end{array} \text{ or } \begin{array}{c} COOH \\ | \\ COOH \end{array}, 2\,H_2O$$

We both satisfy the properties of the acid, and the valencies of its atoms. This formula, showing the existence of two carboxyl groups in a molecule of the acid, suggests that the acid must be dibasic, and we find that this is the case; oxalic acid forms two series of salts, the normal and the acid, represented in the case of potassium salts by the formulæ

$K_2C_2O_4$, H_2O	and	KHC_2O_4, H_2O
normal potassium oxalate.		acid potassium oxalate.

This fact alone would make us infer that the doubled formula, $(CO_2H)_2$, $2\,H_2O$, must be used to represent the body.

84. Chlorine, hydrochloric acid and nitric acid have no action on oxalic acid, but it is readily oxidised to carbon dioxide and water by potassium permanganate or manganese dioxide and sulphuric acid.

Exp. 40.—Take a solution of oxalic acid, add a little dilute sulphuric acid, and warm it to 60°. Run in a few c.c. of potassium permanganate solution. This salt is decolorised, and bubbles of a gas are given off, which is proved to be carbon dioxide by lime water. Repeat the experiment using manganese dioxide instead of potassium permanganate. The manganese dioxide dissolves, and the oxalic acid is again oxidised to carbon dioxide and water. In each case manganous sulphate should be proved to be in the solution.

Heat decomposes oxalic acid; first it splits off water and then decomposes further into a mixture of carbon monoxide and dioxide, and water. The action of strong sulphuric acid is similar, and the oxalic acid splits up into a mixture of carbon monoxide and dioxide, the water being retained by the sulphuric acid. The decomposition may be represented by the equation,

$$(COOH)_2, 2\,H_2O = CO_2 + CO + 3\,H_2O$$

Exp. 41.—Take a small flask fitted with thistle funnel and delivery tube (Fig. 5). Place in the flask about 2 grammes of oxalic acid and cover with excess of strong sulphuric acid. Heat and collect the gas over water saturated with carbon dioxide. Measure the volume collected, transfer it to caustic potash solution, and let it stand. The gas is about half absorbed, and the residue burns with a light blue flame, forming carbon dioxide. Hence the gases, carbon dioxide, and monoxide are evolved in approximately equal volumes.

Oxalic acid forms a large series of salts, of which the most useful and characteristic are the normal and acid potassium oxalates already noticed, salt of lemon and sorrel, KHC_2O_4, $H_2C_2O_4$, $2\,H_2O$, and calcium oxalate, CaC_2O_4, which is insoluble in acetic acid, but soluble in hydrochloric acid.

85. There are many modes of preparing oxalic acid, perhaps the most interesting are:

(i) The action of heat on sodium formate, when hydrogen is given off and sodium oxalate is formed. This may be expressed in equation form thus:

$$2\,HCOONa = H_2 + (COONa)_2$$

(ii) The action of carbon dioxide on sodium at 360°. [Potassium can only be used in a weak solution in mercury, 2 per cent. potassium amalgam.] This may be summarised in an equation,

$$2\,CO_2 + 2\,Na = (COONa)_2$$

(iii) Oxalic acid is generally prepared from carbohydrates thus:

(*a*) By the action of nitric acid on sugar.

Exp. 42.—Boil some sugar with nitric acid for some time in a small flask. Crystals separate out which should be recrystallised from water. The crystals are oxalic acid.

(*b*) By the action of hot caustic potash on sawdust or other forms of woody tissue. The mixture is fused in shallow iron pans, boiled out with water, and the oxalic acid crystallised out on acidification.

86. When milk goes sour, or when sugar is allowed to ferment in neutral solution under the action of Bacillus lactis, an organism which produces souring of milk, a characteristic acid, *lactic acid*, is formed.

If zinc oxide is used to keep the solution neutral, crusts of a crystalline zinc salt are formed. These crusts are suspended in water and precipitated by means of sulphuretted hydrogen. On evaporation an oily liquid is left, with the percentage composition and molecular weight represented by $C_3H_6O_3$; this liquid is lactic acid. A similar body, *sarcolactic acid*, is found in muscular tissue.

87. Lactic acid acts on bases substituting one atom of hydrogen by one atom of a monovalent element, and when heated with lime it splits off carbon dioxide, and forms alcohol. Probably then it is an acid with a carboxyl group, $C_2H_5O\,.\,COOH$. Hydrobromic acid substitutes one bromine atom for one hydroxyl group, forming a derivative of the corresponding acid of the acetic series with three carbon atoms, viz.: *monobrom-propionic acid*. Hence there is probably a basic or alcoholic hydroxyl group in the molecule, and we may write it $C_2H_4(OH)\,.\,COOH$. This is confirmed by the fact that phosphorus pentachloride substitutes two hydroxyl groups by two chlorine atoms, so that lactic acid may be called a *hydroxy* or *oxy-propionic acid*.

When we come to draw out the possible formulae we find that there are two possible lactic acids, viz.:

$$\underset{\beta}{CH_3}\underset{\alpha}{CH}(OH)COOH \quad \text{and} \quad \underset{\beta}{CH_2}(OH)\underset{\alpha}{CH_2}COOH$$

To remember which is which we adopt the plan of lettering the carbon atoms from the group which gives the body its name, in this case the carboxyl group gives the body the name of acid so that the carbon atoms are lettered a, β, γ, etc., starting from the one attached to the carboxyl group.

Then the former acid becomes α-hydroxy propionic acid, and the latter β-hydroxy propionic acid.

88. We can prepare the two acids by different methods which leave no doubt as to the identity of the acid prepared, thus to prepare the α-acid, we act upon aldehyde with hydrocyanic acid as mentioned in § 64.

$$CH_3CHO + HCN = CH_3CH(OH)CN.$$

The action of dilute acids converts this oxycyanide into lactic acid and an ammonium salt. The methyl group can only be changed by substituting its hydrogen, and no such substitution can be observed in this case. The acid prepared must be the α-lactic acid, $CH_3CH(OH)COOH$.

We can also prepare α-lactic acid from propionic acid, CH_3CH_2COOH, by acting first with chlorine which substitutes chlorine for hydrogen in the α-position forming α-chlorpropionic acid, $CH_3CHClCOOH$, following this by the substitution of hydroxyl for chlorine by the action of potash.

These two methods of preparation are both general for oxy-acids. α-lactic acid, sometimes called ethylidene lactic acid, is found to be identical with the natural fermentation lactic acid. It is a thick hygroscopic syrup which gives off water when heated, forming an anhydride. It is split up by dilute acids to a mixture of aldehyde and formic acid, and it is oxidised to acetic and carbonic acids, both of which reactions confirm the suggested formula of α-lactic acid.

89. The chief difference between sarcolactic and ordinary lactic acid is that the former is optically active and dextro-rotatory, while the latter is optically inactive. The latter is, however, half converted into the sarcolactic variety by the action of the blue mould, Penicillium glaucum, while the other half is used up by the mould. When separated, the ordinary inactive acid is found to be a mixture of equal parts of the dextro-rotatory sarcolactic acid and a laevo-rotatory acid of equal rotatory power.

90. The β- or ethylene lactic acid, $CH_2(OH)CH_2COOH$ can be prepared from glycerin by several methods which are beyond tho scope of this volume. Briefly, they consist in substituting chlorine for hydrogen in the β-position, followed by the substitution of hydroxyl for chlorine. The first step is more difficult than tho corresponding step in the formation of the *a*-acid. It forms no anhydride on heating. It is oxidised with the formation of carbonic and oxalic acids.

91. When wintergreen oil is boiled with caustic potash, in order to obtain methyl alcohol, and the caustic potash, solution is acidified with hydrochloric acid, a silky white precipitate is formed. This precipitato dissolves readily in alkalies to form one series of salts only, and is an acid, *salicylic acid.* It has the percentage composition and molecular weight represented by the formula $C_7H_6O_3$.

When heated with lime, phenol, C_6H_5OH, is formed and chalk is left, exactly what we should expect from a carboxyl derivative of phenol, $C_6H_4(OH)COOH$; in fact it is possible to insert a carboxyl group into phenol by passing through phenol sulphonic acid, $C_6H_4(OH)SO_3H$, and phenol cyanide, $C_6H_4(OH)CN$. Salicylic acid is a colourless crystalline solid, almost insoluble in water but soluble in alcohol. It acts as a preservative of fermentable substances, and is used in medical practice.

Exp. 43.—(*a*) Heat a little salicylic acid with quicklime in a small test tube and notice the smell of phenol.

(*b*) Take some salicylic acid and pour some caustic potash solution on it, it readily dissolves; add some dilute hydrochloric acid, the acid is precipitated.

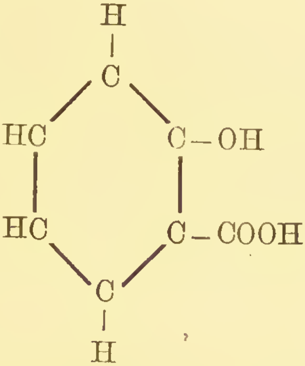
(*c*) To a solution of salicylic acid in a minimum quantity of alkali add some ferric chloride solution. A violet colour is formed.

(*d*) Add some bromine water to some salicylate solution, a white precipitate is formed.

Salicylic acid is prepared commonly by adding to phenol one equivalent of caustic soda, evaporating to dryness, heating tho powdered mixture to 130°, and passing in carbon dioxide. Salicylic acid and phenol are formed; the action may be represented by the equation:

$$\underset{\text{sodium phenol}}{2\,C_6H_5ONa} + CO_2 = \underset{\text{sodium salicylate}}{C_6H_5ONaCOONa} + C_6H_5OH.$$

Three salicylic acids are known, but the one prepared in this way and used for preservative purposes is represented by the formula

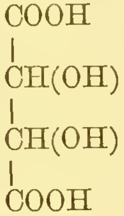


in which the hydroxyl and the carboxyl groups are attached to adjacent carbon atoms of the benzene ring. Such a compound is called an *ortho*-compound and salicylic acid is *ortho-salicylic acid.*

92. When the juice of ripe juicy fruits is evaporated, crystals generally separate mixed with sugar. The crystals dissolve in water, and may be purified by recrystallisation in presence of dilute sulphuric acid or carbonic acid which make the crystals less soluble.

However, in the natural fermentation of grape juice carbon dioxide is formed which causes the precipitation of the same insoluble crystalline substance, *tartar*, which yields potassium carbonate on ignition. The body is recrystallised and forms *cream of tartar*. When heated it chars and forms potassium carbonate, so it appears probable that the original body is a potassium salt of an organic acid. Cream of tartar is dissolved in water, and precipitated as a lead or calcium salt, which is suspended in water and decomposed by sulphuretted hydrogen in the former case and by sulphuric acid in the latter. The solution is evaporated and deposits crystals of an acid body of a composition represented by $C_4H_6O_6$ called *tartaric acid.*

93. Tartaric acid forms two series of salts, and two only, with different amounts of caustic potash solution, so that it is probably a dibasic acid, containing two carboxyl groups. It is acted on by hydrobromic acid with the substitution of two bromine atoms for two hydroxyl groups, so that it probably contains two alcoholic hydroxyl groups. The best way in which a formula can be arranged to agree with this is



$$\begin{array}{l} \text{COOH} \\ | \\ \text{CH(OH)} \\ | \\ \text{CH(OH)} \\ | \\ \text{COOH} \end{array}$$

The presence of so many hydroxyl groups is accompanied by an instability under the action of heat, sulphuric acid, and oxidising agents, even silver salts being reduced by the acid.

Exp. 44.—(*a*) Heat some crystals of tartaric acid alone and with concentrated sulphuric acid, and notice the decomposition products.

(*b*) Shake up a silver solution with ammonia and potash as in Exp. 30, and add some cream of tartar solution. Warm and observe the silver mirror.

The two tartrates of potassium are of interest, the normal salt, $K_2C_4H_4O_6, \frac{1}{2}H_2O$, being soluble, and the acid salt, cream of tartar, $KHC_4H_4O_6$, being rather insoluble in water. Rochelle salt, a double tartrate of sodium and potassium, $KNaC_4H_4O_6, 4H_2O$, is also useful on account of its solubility.

94. The tartrates of the heavy metals are interesting as they are insoluble in water but soluble in cream of tartar solution, with formation of soluble double tartrates. These double tartrates are also soluble in excess of alkali, so that they prevent the precipitation of these metals by alkalies.

Use is made of this property in making up an alkaline solution of a copper salt, *Fehling's solution*, and in making up soluble preparations of iron and of antimony.

Exp. 45.—(*a*) To a solution of a potassium salt add a solution of tartaric acid, and rub the inside of the containing vessel with a glass rod. The insoluble acid salt, hydrogen potassium tartrate, cream of tartar separates out.

(*b*) To a solution of ferric chloride add tartaric acid in excess, and then add excess of ammonia solution. The solution turns brown but no precipitate of ferric hydroxide is formed.

(*c*) To a solution of copper sulphate add Rochelle salt and then caustic potash in excess. No precipitate appears even on boiling, though the solution turns to the blue colour characteristic of alkaline solutions of copper.

CHAPTER IX.

ETHEREAL SALTS. SAPONIFICATION.

95. We have just seen that wintergreen oil is decomposed by alkalies yielding methyl alcohol, *i.e.* an organic base, and salicylic acid, an organic acid. Many other natural oils and fats are similarly decomposed, yielding other alcohols and other acids. It would be of interest to study the formation and properties of a few salts of organic bases and organic acids, *i.e. ethereal salts* or *esters.*

We might at first expect that the resemblance between organic and inorganic acids and bases would be so complete that mere addition of an alcohol to an acid would cause neutralisation, accompanied by the formation of an organic salt and water, but this is not generally the case. In order to form a salt we require the presence of a dehydrating agent in some form, the two generally used being concentrated sulphuric acid or hydrochloric acid gas.

Exp. 46.—Fit a distilling flask with a thermometer and condenser, as in Fig. 3. Make a mixture of 50 c.c. alcohol (methylated spirit), 32 c.c. of glacial acetic acid, and 9 c.c. of strong sulphuric acid, and pour it into the flask. Warm the liquid and collect all liquid coming off below 100°. Pour the distillate into water and shake well: allow to separate, and pour off, separate or pipette off the more oily upper layer. Redistil this upper layer from solid calcium chloride and collect the fraction, boiling about 74—75.° It is a pleasant smelling liquid, *acetic ester.*

96. Acetic ester is a colourless liquid with a pleasant fragrant smell, somewhat like that of apples. Its percentage composition and molecular weight are represented by the formula $C_4H_8O_2$. By the action of concentrated caustic potash solution it is split up into ethyl alcohol, which distils off, and potassium acetate, which remains in solution. This suggests that the body must be considered as *ethyl acetate*, with the formula $CH_3COOC_2H_5$. It is fairly soluble in water (1 in 12), and on standing the water becomes strongly acid from formation of free acetic acid. This decomposition by water, or hydrolysis, gives one explanation of the non-formation of the salt by the action of the free acid on the alcohol, since the water tends to split up the salt as soon as it formed. The equation is generally written thus:

$$CH_3COOH + C_2H_5OH \rightleftarrows H_2O + CH_3COOC_2H_5$$

The two arrow heads indicate that the direction of the change depends upon the relative proportions of the products, and on the conditions of the reaction.

97. We have already seen that glycerin, an alcohol, is obtained from fat in the process of soap-making, and we may now investigate the whole change and the nature of fats.

Exp. 47.—Boil some suet with a dilute solution of caustic potash until it is mostly dissolved. Pour off the clear liquid, and add to it an excess of hydrochloric acid. There is an immediate white precipitate of flocks of a fatty substance. Collect some of the precipitate on a filter paper. Mix some of the precipitate with water; it is insoluble. Add potash solution, the precipitate dissolves, and is again precipitated by the action of an acid. It is probably, therefore, an acid or acids.

Examination of the flocks prepared in this way from different animal fats shows that they are mixtures, and it is possible to squeeze out by pressure a yellow oil, and leave a white wax-like solid.

The yellow oil consists for the most part of an oil represented by the formula $C_{17}H_{33}COOH$, and called *oleic acid*.

The white solid differs in composition with its source. Thus from hard fat and Shea butter its composition is represented by $C_{17}H_{35}COOH$, called *stearic acid*, and from softer fats and Japanese wax the composition is represented by $C_{15}H_{31}COOH$, called *palmitic acid*.

The last two acids are paraffins with a carboxyl group substituted for hydrogen, and the first is an olefine with one pair of trivalent carbon atoms or a double bond.

98. The properties of palmitic and stearic acids are so similar that they are generally considered together. They are colourless fatty bodies, melting at 61° and 71°, respectively. They are insoluble in water, soluble in alcohol, benzene, etc., and in solutions of alkalies. They combine with bases to form salts, the *soaps*. The soluble alkali salts are soluble in pure water, but insoluble in salt water.

Exp. 48.—Make a solution of soap in water and add to it some salt. The soap comes out of solution in the form of flocks, which rise to the surface. Filter off some of the flocks and boil them with water; they are soluble in pure water, so that they are not fatty acids.

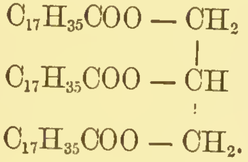
The soaps of the alkaline earths, calcium and magnesium especially, are insoluble in water, and are precipitated by the addition of soap solution to hard water. This precipitation is quantitative, and is used for the estimation of hardness of water.

Soap solution has a curious effect on the surface tension of fats and oils, so that finely divided particles of fats do not tend to run together in a soapy solution. Such an intimate mixture of fat particles and water is termed an emulsion, and the cleansing properties of soap are due to the formation of an emulsion of any particles of grease by the action of the soapy water.

The sodium soaps are harder than the potassium soaps, so that the latter are generally called *soft* soaps.

99. Since glycerin and fatty acids are prepared by splitting fats by the action of caustic potash, we believe the

common fats are compounds of glycerin with the acids, palmitic, stearic, and oleic, and since glycerin is a triad base, we should expect the formula of the stearic acid fat to be



$$\begin{array}{l} C_{17}H_{35}COO - CH_2 \\ \qquad\qquad\qquad\quad | \\ C_{17}H_{35}COO - CH \\ \qquad\qquad\qquad\quad | \\ C_{17}H_{35}COO - CH_2. \end{array}$$

This agrees with the percentage composition of this fat, and it is called *stearin* or *tristearin*. Similar formulae are given to *tripalmitin* and *triolëin*, *i.e.* $(C_{15}H_{31}COO)_3C_3H_5$ and $(C_{17}H_{33}COO)_3C_3H_5$, respectively.

The process of splitting a neutral fat by the action of a base, forming a soap and glycerin is termed *saponification*, but the term is extended to include the splitting of a neutral body into base and acid generally.

100. Palmitic and stearic acids being paraffins with a carboxyl group substituted for hydrogen are members of the acetic series, and it is instructive to compare the properties of the higher and lower acids; their changes of melting point, boiling point, solubility in water, etc.

Just as it is possible to make an ethyl ester from acetic acid, so it is possible to do the same with palmitic and stearic acids, by passing hydrochloric acid gas into an alcoholic solution of the acids. These esters, represented by the formulae

$$C_{15}H_{31}COOC_2H_5 \text{ and } C_{17}H_{35}COOC_2H_5$$

are crystalline bodies melting at 24° and 33°, respectively.

CHAPTER X.

CYANOGEN COMPOUNDS.

101. We have now to deal with a very important class of organic bodies, the *cyanogen compounds*, which contain nitrogen combined with carbon. We have already noticed one important use of these bodies in the synthesis of organic acids.

When electric sparks are passed through a mixture of acetylene and nitrogen they partly combine to form a gas which smells of bitter almonds, and is soluble in caustic potash solution. The gas is obtained purer from the solution in caustic potash by the action of dilute sulphuric acid.

The gas is more conveniently obtained from bitter almonds themselves.

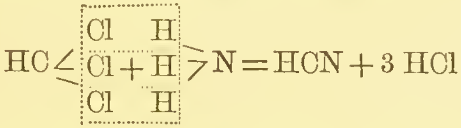
Exp. 49. Pound some bitter almonds in a mortar, add water and mix them well up; allow the mixture to stand in a warm place. After a few hours place the mixture in a flask fitted with a condenser (Fig. 8) and distil. Be careful to do the distillation in a draught chamber, and not to inhale the fumes.

The distillate contains a volatile acid, having the percentage composition and molecular weight represented by the formula HCN, and called *hydrocyanic* or *prussic acid.* The formation of the acid is accompanied by the formation of oil of bitter almonds or benzaldehyde and glucose, and these are all derived from a compound of the three bodies, a glucoside, *amygdalin*, $C_{20}H_{27}NO_{11}$, which may be dissolved out of the almonds by cold water. The equation which represents the reaction is:

$$\underset{\text{amygdalin}}{C_{20}H_{27}NO_{11}} + 2\,H_2O = \underset{\text{benzaldehyde}}{C_6H_5 - CHO} + 2\,\underset{\text{glucose}}{C_6H_{12}O_6} + HCN$$

102. To obtain the pure acid, the dilute solution is mixed with calcium chloride and distilled, when it is found to form a colourless liquid solidifying at -15° and boiling at $26{\cdot}5^\circ$. It has a characteristic smell of bitter almonds or laurel leaves, and is one of the most poisonous bodies known, as regards animal life, either in a state of vapour or in solution. It burns in air when lighted. Hydrocyanic acid is soluble in water, and combines with bases to form salts in which the one hydrogen atom is replaced by the metal of a base.

One of the most interesting syntheses of hydrocyanic acid is by the action of chloroform on ammonia under pressure. This synthesis leaves little doubt that ordinary prussic acid has both the nitrogen and the hydrogen atom in direct combination with the carbon atom. The mechanism of this reaction may be demonstrated thus:



$$\mathrm{HC}\leqslant\boxed{\begin{matrix}\mathrm{Cl} & & \mathrm{H}\\ \mathrm{Cl} & + & \mathrm{H}\\ \mathrm{Cl} & & \mathrm{H}\end{matrix}}\geqslant\mathrm{N} = \mathrm{HCN} + 3\,\mathrm{HCl}$$

This mode of formation of the acid justifies the use of a triple bond between the nitrogen and carbon atoms to indicate that the nitrogen atom is playing the part of three monovalent atoms or groups, $\mathrm{HC}\equiv\mathrm{N}$.

103. On mixing caustic potash with excess of hydrocyanic acid and evaporating the solution we obtain a colourless deliquescent solid, *potassium cyanide*, KCN. The salt is very soluble in water and also but to a less extent in alcohol. It is a very poisonous salt. As hydrocyanic acid is a weak acid, potassium cyanide smells of prussic acid since the carbon dioxide of the air forms a strong enough acid in presence of moisture to decompose the salt.

Potassium cyanide precipitates other metallic cyanides from solution, *e.g.* silver and mecuric cyanides, AgCN and $\mathrm{Hg(CN)_2}$, but these cyanides readily dissolve in excess of the potassium salt though they are insoluble in water. The explanation of this change of solubility is that double salts of silver or mercury and potassium are formed, which are soluble in water.

Exp. 50.—(*a*) To a solution of silver nitrate add potassium cyanide solution. A white precipitate is formed of silver cyanide, $AgCN$; as excess of the cyanide solution is added the precipitate dissolves, forming the double salt, $AgCN, KCN$.

(*b*) Add the solution of silver nitrate to the cyanide. Any precipitate seen is immediately dissolved until just half the acid is present as the silver salt and half as the potassium salt; at this point all is in solution, but the addition of a few drops more of silver solution causes a precipitate of silver cyanide.

The equations which represent these reactions are:

$$\left\{\begin{array}{l} KCN, Aq + AgNO_3, Aq = AgCN + KNO_3, Aq \\ AgCN + KCN, Aq = AgCN, KCN, Aq \\ AgCN, KCN, Aq + AgNO_3, Aq = 2\,AgCN + KNO_3Aq \end{array}\right.$$

104. Just as mercuric oxide is split up by heat into a mixture of mercury vapour and oxygen so mercuric cyanide is split up into a mixture of mercury vapour and another gas, which smells very like prussic acid, and burns with a lavender flame. This gas has the molecular composition represented by the formula C_2N_2, and is called *cyanogen.*

The equation which represents the greater part of the reaction is $$Hg(CN)_2 = Hg + (CN)_2$$ which may be compared with the corresponding equation for the decomposition of mercuric oxide:

$$2\,HgO = 2\,Hg + O_2$$

The gas is so intensely poisonous that it should only be prepared with the greatest precautions.

105. The existence of cyanogen enables us to make the story of hydrocyanic acid complete by showing the resemblance in properties between the *element chlorine* and the *compound radicle cyanogen.*

(*a*) Cyanogen combines with metals directly to form cyanides; in the case of potassium we may compare the action with that of chlorine:

$$\begin{aligned} 2\,K + (CN)_2 &= 2\,KCN \\ 2\,K + Cl_2 &= 2\,KCl \end{aligned}$$

(*b*) Cyanogen forms a hydride which has acid properties and forms salts from which the hydride is prepared by the action of less volatile acids. This is also the case with chlorine:

$$\begin{aligned} KOH + HCN &= KCN + H_2O \\ KOH + HCl &= KCl + H_2O \end{aligned}$$

(*c*) The free radicle forms its molecules by doubling, like chlorine: compare $(CN)_2$ and Cl_2

(*d*) The action of cyanogen on a caustic alkali is similar to that of chlorine, involving both an oxidation to the state of cyanic acid and a reduction to the state of hydrocyanic, thus:

$$\begin{aligned} 2\,KOH + (CN)_2 &= KCN + KCNO + H_2O \\ 2\,KOH + Cl_2 &= KCl + KClO + H_2O \end{aligned}$$

106. One of the most important properties of the cyanides, as we have just seen, is their tendency to form double salts, but in the case of the cyanides of the iron and other metals of Group VIII., these salts are even more characteristic, and are considered as salts of new compound acids.

Exp. 51.—To a solution of ferrous sulphate add potassium cyanide solution. A brown precipitate of ferrous cyanide is seen. Add excess of the potassium salt, and the precipitate gradually dissolves forming a yellow solution. Filter the solution and evaporate down, yellow crystals separate out. These crystals are potassium ferrocyanide.

Potassium ferrocyanide, $4\,KCN$, $Fe(CN)_2$, $3\,H_2O$ or $K_4FeC_6N_6$, $3\,H_2O$, is a most important salt, and it is the chief commercial source of the cyanogen compounds. It is prepared commercially by fusing together potassium carbonate, leather scraps, and iron filings. The melt is dissolved in water and crystallised out. The steps in the process are complicated, but may perhaps be explained thus:

(1) The potassium carbonate, K_2CO_3, is reduced by the carbon of the leather to potassium, which then acts upon the nitrogenous part of the leather to form potassium cyanide, KCN.

(2) The potassium cyanide acts upon the iron in presence of air and water to form ferrous cyanide and caustic potash. We may put this in equation form :

$$4\,KCN + 2\,Fe + 2\,H_2O + O_2 = Fe(CN)_2 + 4\,KOH$$

(3) The ferrous and potassium cyanides react to form potassium ferrocyanide :

$$Fe(CN)_2 + 4\,KCN,\ Aq = K_4FeC_6N_6,\ Aq$$

107. Potassium ferrocyanide dissolves in water, but is insoluble in alcohol. Its reactions are most important.

(1) Concentrated hydrochloric acid substitutes hydrogen for potassium, forming a colourless body represented by the formula $H_4FeC_6N_6$. This must be the acid corresponding to the salt, potassium ferrocyanide, and it is called *hydroferrocyanic acid.* The existence of this acid is confirmed by trying the tests for potassium, ferrous iron and hydrocyanic acid in the salt, as in Exp. 52.

(2) Hot concentrated sulphuric acid decomposes the salt forming sulphates of potassium, ammonium and iron, and giving off carbon monoxide. An equation may be given:

$$K_4FeC_6N_6, + 8(H_2SO_4,\ 2\,H_2O)$$
$$= 4\,KHSO_4 + FeSO_4 + 3\,(NH_4)_2SO_4 + 6\,CO + 10H_2O.$$

(3) Fairly strong sulphuric acid (H_2SO_4, $4H_2O$) decomposes the salt forming hydrocyanic acid and a double ferrocyanide of potassium and iron, $K_2Fe(FeC_6N_6)$. This is the reaction used for preparing hydrocyanic acid commercially.

(4) Dilute sulphuric acid completely decomposes the salt, forming potassium and ferrous sulphates and hydrocyanic acid. An equation may be given:

$$K_4FeC_6N_6 + 5H_2SO_4, Aq = 4KHSO_4Aq + FeSO_4Aq + 6HCN$$

(5) When heated alone a mixture of potassium cyanide and ferrous carbide is formed, and nitrogen gas is given off, thus :

$$K_4FeC_6N_6 = 4\,KCN + FeC_2 + N_2$$

The loss of cyanide is avoided if the ferrocyanide is mixed with potassium carbonate in formula weights before heating, but the product contains cyanate, thus :

$$K_4FeC_6N_6 + K_2CO_3 = 5\,KCN + KCNO + Fe + CO$$

(6) When heated with an oxidising agent such as peroxide of lead or manganese it is oxidised to potassium cyanate. The reaction is just the same if potassium cyanide is used instead of potassium ferrocyanide, thus:

$$2\,KCN + PbO_2 = 2\,KCNO + Pb$$

This explains the powerful reducing action of potassium cyanide.

(7) Chlorine oxidises potassium ferrocyanide in solution by removing one atom of potassium from it. The salt formed is called potassium ferricyanide, and is usually given the double formula, $K_6Fe_2C_{12}N_{12}$, though there does not seem to be any adequate reason for preferring this formula to the simpler, $K_3FeC_6N_6$. The equation representing its formation may be given:

$$2\,K_4FeC_6N_6,\ Aq + Cl_2 = 2\,K_3FeC_6N_6,\ Aq + 2\,KCl,\ Aq$$

Exp. 52.—To solutions of potassium cyanide and potassium ferrocyanide add silver nitrate and ferric chloride solutions, and compare the results. The ferrocyanide does not give the cyanide reactions. To solutions of ferrous sulphate and potassium ferrocyanide add ammonium chloride and ammonia, the ferrocyanide does not give the ferrous tests. The ferrocyanide is not an ordinary double salt.

Heat some potassium ferrocyanide with concentrated sulphuric acid and collect the gas given off over water. It burns with a blue flame, forming carbon dioxide, and is carbon monoxide.

To solutions of potassium ferrocyanide and ferricyanide add ferrous and ferric salts. Note that no precipitate is formed of ferric ferricyanide, and that all the other mixtures give blue precipitates; ferric ferrocyanide is Prussian blue.

108. The organic cyanides, also called nitriles, have already been mentioned as of great importance in the synthesis of organic acids. They are prepared by two separate methods.

(i) By the action of potassium cyanide on the haloid derivatives of the hydrocarbons in alcoholic solution, or by the distillation of the acid sulphates of the alcohols or the sulphonates of the benzene compounds with potassium cyanide or ferrocyanide. Equations may be given:

$$CH_3I + KCN = CH_3CN + KI$$
$$C_6H_5.KSO_3 + KCN = C_6H_5CN + K_2SO_3$$

It has already been noticed that this reaction is characterised by the addition of one carbon atom to the molecule.

(ii) By the removal of water from the ammonium salts of the organic acids by phosphorus pentoxide. Thus, in the case of ammonium acetate, methyl cyanide is formed, $CH_3COONH_4 - 2\,H_2O = CH_3CN$. No change in the number of carbon atoms is noted here.

We have already noted the formation of oxy-cyanides by the action of hydrocyanic acid on the aldehydes.

As already seen, water, dilute acids, and alkalies saponify the cyanides into ammonia and an organic acid. In the case of methyl cyanide, ammonium acetate is reformed:

$$CH_3CN + 2\,H_2O = CH_3COONH_4$$

Nascent hydrogen converts the cyanides into a new class of bodies considered in the next chapter, the *amines*. Thus methyl cyanide is converted into ethylamine.

CHAPTER XI.

AMIDO COMPOUNDS.

109. An examination of products of putrefaction, herring pickle, fungi, and many other bodies, by heating them with solutions of caustic alkali, causes them to give off substances with a characteristic blended smell of ammonia and fish. These bodies readily dissolve in water, to which they impart their smell and the property of turning litmus blue. Their solutions resemble ammonia solution in being neutralised by acids with the formation of colourless, crystalline salts.

Similar bodies are formed when the haloid derivatives of the hydrocarbons are heated with an alcoholic solution of ammonia.

Thus when ethyl iodide, C_2H_5I, is heated with an alcoholic solution of ammonia under pressure a solid residue is obtained after evaporation, which is a mixture of five substances which can be separated only by a somewhat complicated method. These substances are found to have the formulae, $NH_3(C_2H_5)I$, $NH_2(C_2H_5)_2I$, $NH(C_2H_5)_3I$ and $N(C_2H_5)_4I$ respectively, and are mixed with ammonium iodide, NH_4I.

110. From the appearance of these formulae we should expect that the substances would resemble ammonium salts and be decomposed by caustic potash solution. It is found that caustic potash does decompose the first three, forming potassium iodide, and liberating gases which resemble ammonia in properties and may be considered as ammonia, in which hydrogen atoms are replaced by the radicle ethyl. Such bodies are called *amines*, and these are *ethylamines*, their salts being called *ethyl-ammonium salts.*

Thus the first of the above bodies, $NH_3(C_2H_5)I$ is called ethylammonium iodide, and yields under the action of potash, ethylamine, $NH_2C_2H_5$. The second, $NH_2(C_2H_5)_2I$, is called diethylammonium iodide and yields $NH(C_2H_5)_2$ diethylamine. The third, $NH(C_2H_5)_3I$ is triethylammonium iodide and yields triethylamine $N(C_2H_5)_3$. The fourth, which is not decomposed by potash, is $N(C_2H_5)_4I$, tetraethylammonium iodide.

111. The formation of these bodies is very interesting, and takes place in stages, combination preceding decomposition. To take the first case, some ammonia probably combines directly with the ethyl iodide to form ethylammonium iodide, this is acted upon by the excess of ammonia with the formation of ammonium iodide and ethylamine; the same changes take place with the ethylamine and diethylamine produced, and so on. Equations may be conveniently used to represent these changes:

$$\left\{\begin{array}{ll} NH_3 + C_2H_5I & = NH_3(C_2H_5)I \\ NH_3(C_2H_5)I + NH_3 & = NH_4I + NH_2C_2H_5 \end{array}\right.$$

$$\left\{\begin{array}{ll} NH_2C_2H_5 + C_2H_5I & = NH_2(C_2H_5)_2I \\ NH_2(C_2H_5)_2I + NH_3 & = NH_4I + NH(C_2H_5)_2. \end{array}\right.$$

112. Two other important methods are available for preparing amines.

(2) By the action of nascent hydrogen on a nitro compound of a hydrocarbon, when two hydrogen atoms are substituted for two oxygen atoms, a rather unusual exchange, though not quite unexpected, since two atoms of hydrogen can combine with two atoms of oxygen to form hydrogen peroxide, H_2O_2. To take the case of ethylamine, ethyl iodide is digested with silver nitrite and nitro ethane is formed. Using an equation:

$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI$$

By the action of nascent hydrogen (iron and acetic acid may be used) this is reduced to ethylamine, $C_2H_5NH_2$.

(3) The third method has been already mentioned, viz., the action of nascent hydrogen on a cyanide or nitrile. In this case, the carbon atom of the cyanide forms part of the

hydrocarbon radicle after reduction, so the ethylamine is made by the reduction of methyl cyanide, thus:

$$CH_3CN + 2\,H_2 = CH_3CH_2NH_2$$

It will be noted that the last two methods only give us one amine at a time, so they can be readily identified. All these reactions, too, seem to point to a close connection between the classes of nitrogen derivatives of organic bodies.

113. The ethylamines are liquids with a fishy smell of ammonia. They combine with acids to form salts, and their chlorides are like ammonium chloride in combining with platinic chloride to form platino-chlorides, *e.g.* $(NH_3C_2H_5)_2PtCl_6$, from ethylamine, $NH_2C_2H_5$. These salts are used to determine the molecular weights of the amines.

The salts are saponified by caustic potash, except tetraethlyammonium iodide, $N(C_2H_5)_4I$, which however yields a free base tetraethylammonium hydroxide $N(C_2H_5)_4OH$ by the action of moist silver hydroxide.

Just as ammonia is oxidised by nitrous acid to water and free nitrogen, so the amines are oxidised by nitrous acid to alcohols and free nitrogen. Thus ethylamine yields ethyl alcohol when heated with nitrous acid.

$$NH_2(C_2H_5) + HNO_2 = C_2H_5OH + N_2 + H_2O$$

Compare

$$\begin{aligned} NH_3 \qquad + HNO_2 &= HOH + N_2 + H_2O \\ &= N_2 + 2\,H_2O \end{aligned}$$

A very characteristic reaction of many amines is the production of an isonitrile smell on heating with chloroform and caustic potash, see Exp. 18.

114. When we attempt to substitute the phenyl group, C_6H_5-, for hydrogen in ammonia by heating monochlorbenzene, C_6H_5Cl, with alcoholic ammonia, no action takes place.

The second method answers better, and on treating nitro-benzene, $C_6H_5NO_2$, with nascent hydrogen, two oxygen atoms are substituted by two hydrogen atoms, and a phenylamine, $C_6H_5NH_2$, is prepared. This phenylamine is identical with a body found in small quantity in coal tar and the decomposition products of indigo, and separated from them by distillation. It is generally called *aniline* from this indigo body.

Exp. 53.—Into a half litre flask put about 50 grammes of granulated tin and cover it with strong hydrochloric acid. Pour into the flask a few c.c. of nitrobenzene, and shake it up frequently until the nitrobenzene dissolves. When all is dissolved add an excess of caustic soda, fit the flask with a condenser and a tube passing to the bottom of the flask through which steam is blown from a tin can. The distillate separates into two layers, a heavy yellow liquid at the bottom, and a milky layer above. Separate the two layers and examine the heavy liquid, which is aniline.

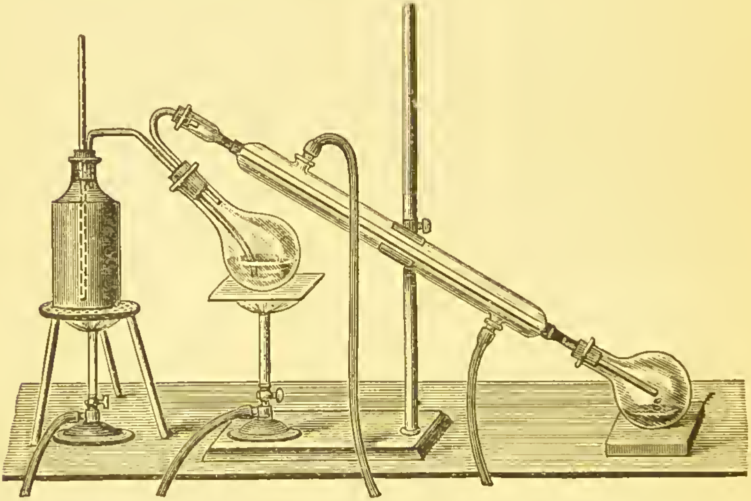


Fig. 12.

Aniline is a colourless liquid of specific gravity, 1·038, when pure; it rapidly turns brown on exposure to the air. It has a characteristic smell, and is slightly soluble in water, 1 in 33. It has no action on litmus, but combines with acids except carbonic to form salts. Aniline is a weaker base than ammonia in the cold, but it displaces the latter at high temperatures, owing to its higher boiling point. It forms a platino-chloride, and it reacts with sulphuric acid and nitric acid in the same way as benzene, viz. when heated with sulphuric acid it forms aniline sulphonic acid and when mixed with nitric and sulphuric acids it forms a nitro body, *nitraniline.*

115. The reactions of aniline with nitrous acid are most characteristic and important. Thus, when heated with nitrous acid and water it forms phenol as ethylamine forms alcohol.

$$C_6H_5NH_2 + HNO_2 = C_6H_5OH + N_2 + H_2O$$

If, however, an alcoholic solution of aniline is treated with nitrous acid the alcohol is oxidised to aldehyde and the aniline reduced to benzene.

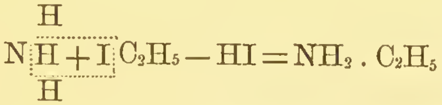
$$C_6H_5NH_2 + HNO_2 + C_2H_6O = C_6H_6 + N_2 + 2\,H_2O + C_2H_4O$$

We find that a complete explanation of these reactions can be given, when we discover that there is an intermediate nitrogen base formed, called *diazo benzene hydroxide,* thus:

$$C_6H_5N\boxed{H_2 + O}NOH = C_6H_5N_2OH + H_2O$$

The characteristic tests for aniline are (i) the isonitrile smell when heated with chloroform and caustic potash, and (ii) the production of a mauve colour by the action of bleaching powder solution.

116. Starting with the mode of formation of the ethylamines from ammonia by the action of ethyl salts, we have considered the amines as derived from ammonia by the substitution of an organic radicle for hydrogen, thus:



$$N\overset{H}{\underset{H}{\boxed{H + I}}}C_2H_5 - HI = NH_2\,.\,C_2H_5$$

Hydrocyanic acid may consequently be considered as a special case in which the group ($\equiv$CH) replaces three atoms of hydrogen of ammonia.

But it is also possible to look at the amines as derivatives of the alcohols in which the group ($-NH_2$), *the* *amido group*, replaces hydroxyl, with the formation of water, thus:

$$C_2H_5\boxed{OH + H}NH_2 - H_2O = C_2H_5NH_2$$

Looked at from this point of view we should expect the other hydroxyl derivatives of the hydrocarbons, viz., the aldehydes and acids, to combine with ammonia and split off water. We find that this is the case, the aldehydes forming the compounds *aldehyde ammonias*, and the acids ammonium salts, and amides, thus:

$$CH_3CH\begin{array}{l}\underline{OH + H}\,|NH_2 - H_2O = \underset{\text{aldehyde ammonia}}{CH_3CH(OH)NH_2}\\ OH\end{array}$$

$$CH_3CO\boxed{OH + H}NH_2 - H_2O = \underset{\text{acid amide}}{CH_3CONH_2}$$

Aldehyde ammonia need not be further considered, so that there only remains the last class, the *acid amides*.

117. To take the simple case of acetic acid, ammonia readily reacts with acetyl chloride, CH_3COCl, to form *acetamide*, CH_3CONH_2, in which the amido group may be looked upon as taking the place of a chlorine atom in the chloride, or the acid group acetyl (CH_3CO-) as taking the place of a hydrogen atom in ammonia.

Exp. 54.—Distil some ammonium acetate in a small retort (Fig. 11). After a time a solid condenses in the neck of the retort, with a smell of mice. This is acetamide.

By heating ammonium acetate it splits off water, and finally forms acetamide, which can be further dehydrated by phosphorus pentoxide to form methyl cyanide (aceto-nitrile), thus:

$$\left\{\begin{array}{ll} CH_3COONH_4 & = CH_3CONH_2 + H_2O \\ CH_3CONH_2 & = CH_3CN + H_2O \end{array}\right.$$

The acid amides are converted back again into ammonium salts, just like the cyanides.

118. The most important amide from the physiological point of view is probably *urea*.

When urine is evaporated down, long rhombic prisms separate out, called urea, which are soluble in alcohol, but not in ether. The crystals melt at 132° and sublime in vacuo. When analysed they are found to be represented by the formula CON_2H_4, or possibly some multiple of that.

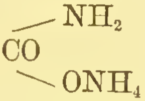
When urea is heated it gives off ammonia. [It forms several compounds in succession, biuret, cyanuric acid, and cyanic acid.]

Alkalies decompose urea, forming a carbonate of the alkali, and setting free ammonia.

119. Hence since urea splits up into carbon dioxide and ammonia it is possibly connected directly with them.

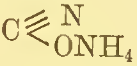
Exp. 55.—Fill a jar with ammonia gas and another with carbon dioxide, and place them mouth to mouth. They combine forming a white solid.

The white solid formed by the direct combination of ammonia and carbon dioxide is not ammonium carbonate, though it is readily converted into that salt by the action of water. It may be represented by the formula $CO_2, 2\,NH_3$. It has been proved that the two nitrogen atoms are not situated similarly in the molecule, so that the formula must be written as that of an ammonium salt, *ammonium carbamate.*



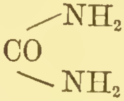
$$\mathrm{CO}\begin{cases}\mathrm{NH_2}\\ \mathrm{ONH_4}\end{cases}$$

Phosphorus pentoxide dehydrates this salt, forming urea, which may thus be :



$$\mathrm{C}\begin{cases}\equiv\mathrm{N}\\ \mathrm{ONH_4}\end{cases}$$

or



$$\mathrm{CO}\begin{cases}\mathrm{NH_2}\\ \mathrm{NH_2}\end{cases}$$

The first formula represents it as ammonium cyanate, the second as the amide of carbonic acid, *carbamide.*

[Urea may be also prepared by the action of phosphorus pentoxide, or a temperature of 135°, on ammonium carbonate.]

120. Ammonium cyanate is readily made by passing ammonia and cyanic acid into dry ether, and it is not the same as urea, however, on being warmed, it suffers an

isomeric transformation, and is converted into urea. This change was first observed by Wöhler in 1828, and it marks the first synthesis of an organic compound from inorganic substances.

We can confirm the carbamido formula which is left over for urea by the reaction of carbonyl dichloride, $COCl_2$, with ammonia, which gives rise to urea.

$$COCl_2 + 4\,NH_3 = CO(NH_2)_2 + 2\,NH_4Cl$$

121 Urea combines directly with acids to form salts, of which the most characteristic are the nitrate and the oxalate. It is decomposed by nitrous acid with the formation of carbon dioxide, nitrogen and water. Hypochlorites and hypobromites also oxidise urea with formation of the same products; in these reactions the volume of nitrogen given off bears a nearly constant relation to the amount of urea taken, so that it is used for the quantitative estimation of urea.

Mercuric nitrate forms a white precipitate with urea, which is approximately constant in composition, and is represented by $2\,CO(NH_2)_2,\ Hg(NO_3)_2,\ 3\,HgO$. The precipitate removes all the urea from a solution, and so is used in the estimation of urea by Liebig's volumetric method.

With the amines and amides we reach the simplest of the decomposition products of protoplasm, and just touch the fringe of that most important part of our subject, which must be left to future work, viz., the chemistry of protoplasm and its products.

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